

SOIL ORGANIC MATTER

ITS NATURE, ITS ROLE IN SOIL FORMATION AND IN SOIL FERTILITY

2nd ENGLISH EDITION

by

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PREFACE TO THE SECOND ENGLISH EDITION

THE GREAT interest shown in the first English edition of my book *Soil Organic Matter* (Pergamon Press, Oxford, 1961) indicates that much attention is being paid to this subject by many research workers.

I am greatly indebted to those colleagues who have expressed their opinions about the book in reviews published by many journals in different countries and also in letters to the author, and who have, in a friendly way, pointed out its shortcomings. These I have attempted to eliminate in the present edition.

The chapters on the nature of soil organic matter, its role in soil formation and soil fertility, and also its manifold influences on the plant, have been revised and supplemented in the light of recent literature.

The chapter on the nature of humus in the soils of the USSR is supplemented by new data. The great attention paid by research workers to this section of the problem of organic matter and their attempts to reveal the natural laws of humus formation indicate that Russian soil scientists remain faithful to the principles of Dokuchaev's genetic pedology.

The author expresses sincere gratitude to Dr. T. Z. Nowakowski and Dr. A. C. D. Newman who have undertaken the difficult task of preparing the second edition of this book, to Dr. D. S. Jenkinson for his collaboration, and to Pergamon Press for its publication.

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CHAPTER 1

THE MAIN STAGES IN THE HISTORY OF SOIL HUMUS STUDY

CONTEMPORARY ideas on soil humus have developed as the result of many years of study. The reason why the problem of soil humus has received so much attention is explained partly by its wide importance in soil-forming processes and soil fertility and partly by its complexity, which made it necessary to approach the problem from different angles.

Because of the complexity of the soil-humus problem a comprehensive study of this subject therefore requires the participation of pedologists, microbiologists, zoologists, plant physiologists, agronomists, chemists and physical chemists, etc.

The trend of investigations and the development of views on the main aspects of the problem were, at each period, greatly affected by the stage of development of other branches of science.

Characteristic of the history of soil-humus study was the attempt to develop certain important aspects of the subject before sufficient progress had been made in a related discipline. For instance, the study of the formation of humus substances¹ by microbial activity attracted the attention of investigators in the first half of the last century while soil microbiology developed in the second half of the century.

Naturally this "gap" had an effect on the state of the problem of the origin of humus substances. Investigators in the first half of the last century who approached this problem from the chemical angle (chemistry had developed considerably in that period) regarded humus substances as oxidation products of certain plant materials (simple carbohydrates, cellulose, encrusting substances). They tried to reproduce the formation of humus substances chemically by subjecting these materials to the action of acids and alkalis.

¹ *Translators' note.* At the suggestion of Prof. Kononova, the Russian term *gumusovye veshchestva* has been translated in this edition as "humus substances" because it was felt that the translation used in the previous English edition, "humic substances", might be confused with "humic acids".

The history of humus study abounded with similar methodologically unsound attempts to solve the main problems; this resulted in the appearance of controversial and confused ideas on the nature and properties of humus, its origin and the role of humic substances in soil formation and soil fertility. Suffice it to say that many investigators repeatedly questioned the actual existence of humus substances as natural compounds of specific nature.

The complexity of the problem, the presence of a large volume of literature and considerable contradictions in the views of individual investigators all greatly complicate a historical survey of studies on humus. Nevertheless, this task cannot be ignored when one considers that a critical examination of earlier works will help to expose their errors and indicate the correct approach to further investigations.

However, a detailed review of the literature on soil humus will not be attempted here as this has already been done successfully by other authors. Instead we shall restrict ourselves to an examination of the most important works of the individual stages, the sequence of which constitutes the historical development of the science of soil humus.

THE INITIAL PERIOD OF INVESTIGATION

The second half of the 18th and beginning of the 19th century

Instead of considering the early investigations, which merely proposed the confused idea that humus was a soil constituent of great importance in soil fertility, we shall turn directly to works of the second half of the 18th century.

In Wallerius's book (1761), which was the first scientific guide to agricultural chemistry, there were indications of the formation of humus during the decomposition of plants and of certain of its properties—the capacity for absorbing water (hydrophilic nature) and nutrients; humus was thus regarded as a plant food. Lomonosov's publication *The First Principles of Metallurgy or Mining* (1763) belongs to this period. In this work, Lomonosov expressed the view that soils with a high humus content (chernozems?) originate “from the rotting of animal and plant bodies with time”.

During the following years of this period, the problem of chernozem formation attracted the attention of many scientists, who linked its origin either with aquatic vegetation (Pallas), animals (Petzold) or steppe grasses (Güldenstaedt).

In 1782, there appeared a book by the Russian scientist, Komov, called *Agriculture*, which took the form of a guide to general agriculture and to methods of cultivation of the main crops.

In this book the author made striking statements on the role of humus in soil fertility. He associated the more important hydro-physical properties of the soil and its richness in nutrients with the presence of humus. He held the view that "the nutritive juice of plants does not differ at all from animal food" and that "what is still more surprising the nutritive juice of both is produced in the same way, namely, by rotting" (p. 120). Thus, in Komov's book there are certain aspects of the humus theory of plant nutrition developed later by Thaer.

Komov pointed out the importance of organic manures (farmyard manure) for increasing soil fertility and he recommended the wide sowing of perennial grasses. Later, he suggested rotation schemes in which the latter were included. Komov's work thus laid the scientific foundations of the agricultural system which was developed later for Russian conditions by Dokuchaev, Kostýchev, Sovetov, Izmail'skiĭ and Williams.

The obscure ideas on humus substances began to take a more definite form when the latter were isolated from a number of natural products. Achard (1786) appears to have been the first to isolate humus substances from peat by treatment with alkali solutions; with subsequent acidification of the alkali extract, humus substances separated out in the form of a dark amorphous precipitate. Achard noticed that the alkali solutions extracted a larger amount of humus substances from the lower, more humified layers of the peat than from the less-rotted plant residues of the upper layers.

Vauquelin (1797) succeeded in isolating humus substances in the form of an alkali solution from the wood of elm infected with fungi. Later, Thomson (1807) proposed the name of ulmin for these substances.

The isolation of humus substances from decomposing plants, peats and soils by various investigators gave an impetus to the study of their nature and properties. Advances in the development of the natural sciences at the end of the 18th and the beginning of the 19th century, particularly in chemistry and plant physiology, prompted the undertaking of these investigations and in addition determined their direction.

De Saussure (1804) was the first investigator to show that humus substances contain more carbon and less hydrogen and oxygen than the original plant residues. This was an indirect indication of the complexity of the process of humus formation. Although de Saussure showed that plants take up oxygen and carbon dioxide from the air, he nevertheless recognized that plants might utilize humus substances; after isolating the water-

soluble part ("humic extract") from humus, he concluded, from the results of pot experiments, that humus substances are directly assimilated by plants.

As is well known, the theory of the humus nutrition of plants was developed fully by Thaer (1809), who concluded on the basis of the experimental data available at the time that soil fertility was largely dependent on the accumulation in the soil of humus, which he believed was the sole and direct source of plant nutrients. The humus theory of plant nutrition was widely accepted for several decades until the appearance of works by Boussingault (1841) and Liebig (1840), the founders of the theory of the mineral nutrition of plants.

Braconnot's early attempts (1807, 1819) to obtain humus substances artificially by the treatment of carbohydrates and other plant substances with mineral acids also belong to this period. Braconnot gave the name of ulmin to the brown alkali-soluble substance obtained in this way; he considered this substance to be similar to natural ulmin.

Because of lack of knowledge about soil micro-organisms and their participation in the transformation of organic substances in the soil, humus formation was regarded as a purely chemical process.

Thus, by the end of the 18th and beginning of the 19th century the basis of the idea that humus substances are peculiar natural compounds was established and the first steps were taken in the study of their chemical nature and in the elucidation of their role in plant nutrition. At the same time there were faulty methods of obtaining humus substances by the treatment of plant materials with acid and alkali solutions and incorrect ideas that humus formation was a chemical process. Later, these mistakes intensified and resulted in the emergence of erroneous ideas both on the mechanism of the process and on the origin of humus substances.

The next period of soil-humus study is characterized primarily by the development of investigations on its chemical nature.

THE FIRST HALF OF THE 19TH CENTURY

The development of investigations on the chemical nature of humus substances

The beginning of the systematic study of the chemical nature of humus substances was closely linked with the name of Sprengel (1826, 1837), who was the first to give a detailed description and analysis of humic acid. From a quantitative determination Sprengel found that the carbon content of humic acid was 58 per cent. He also described the more impor-

tant properties of humic acid and its salts (humates) and studied the decomposition of humates and their solubility in water; he noted that freshly-precipitated humic acid, washed free from electrolytes, dissolved partially in water (particularly hot water) and that after drying or freezing, the acid was converted into a sparingly soluble form ("humus coal"). In accepting the humus theory of plant nutrition to some degree, Sprengel considered that the differing solubility of the humus was of great importance in soil fertility. Thus, he attributed the high fertility of the soils of southern Europe, in particular, to the presence of humus substances in soluble forms.

Sprengel also established the acid nature of humic acid; he showed that humic acid has a negative charge and is a stronger acid than carbonic acid; it releases silicic acid from silicates. Because of its acid properties, humic acid, in soils rich in bases, combines immediately with the latter. Such a soil remains neutral, contains "sweet" humus and is extremely fertile. If the soil has a low base content it becomes acid in the presence of free humic acids and loses fertility; this phenomenon is observed in peat soils.

Thus, Sprengel made what for that period was a fairly comprehensive study of the nature and properties of humus substances. The methods he used for isolating humic acids and for investigating their chemical nature became generally adopted and have, in some degree, retained their importance right up to the present day. Many of Sprengel's statements (e.g. with regard to acid properties) were developed further by many workers.

Investigations on the nature of humus substances were extended by the well-known Swedish scientist, Berzelius (1806). He found that besides black humus substances (humic acids) there were also humus substances of light-yellow colour, which he detected in a mineral spring at Porla. Later (1833, 1839), he revealed that similar substances in the form of compounds forming salts with iron are precipitated from many iron-containing waters, are present in "natural waters containing ochre and in swampy soils" and can be extracted from soils with water. These newly-discovered humus substances, which Berzelius named crenic and apocrenic acids, were isolated by him as preparations and studied in detail; he regarded apocrenic acid as an oxidation product of crenic acid.

Berzelius distinguished the following humus substances: (1) humic acid soluble in alkali solutions; (2) the inert form—humin, corresponding to Sprengel's "humus coal"; (3) crenic and apocrenic acids.

Berzelius described the separation of the humus substances and also their chemical properties. He gave a most detailed account of crenic and apocrenic acids (methods of isolation, elementary composition and

properties of the salts of ammonia, Ba, Mg, Al, Fe, Mn, Pb, Cu, etc.). A very important property of these salts was established—their great solubility and, therefore, their great mobility compared with the salts of humic acids.

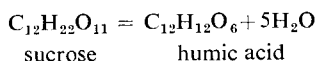
These properties explain the different role of crenic and apocrenic acids in soil-forming processes, in particular, the participation of crenic acids in podzol formation, first reported by Sibirtsev (1900—1901).

Berzelius's investigations also dealt with the productive importance of humus. Like most of his contemporaries, Berzelius accepted the humus theory of plant nutrition and believed that soil fertility was associated with the presence of humus. Accordingly, on the assumption that crops are continually decreasing the amount of humus in the soil, he pointed out the necessity of applying organic manures.

Berzelius's investigations, which he incorporated in the well-known work *Textbook of Chemistry* (1839), were developed further by his contemporaries and followers. The most distinguished of these were his student, Mulder, and the Russian investigator, German. It should be noted that their investigations were also greatly influenced by works on the artificial production of humus substances.

In the first instance, Braconnot (1807, 1819) obtained artificial humus substances from carbohydrates chemically by treating them with acids. Then Boullay (1830) found that on heating glucose with alkalis a dark-coloured liquid formed, from which a brownish flocculent precipitate separated out after the addition of acid. Boullay identified the preparation obtained as ulmic acid.

Later, Malaguti (1835), on the basis of numerous experiments on the artificial production of humus-like preparations from various organic materials and from the results of their analysis, also considered that these substances were identical with natural humus substances. He regarded the mechanism of humification of carbohydrates as a dehydration proceeding as follows:



We shall not mention any of the other works on the artificial production of humus substances here, although it should perhaps be mentioned that their importance was clearly overrated at the time. The artificial humus-like substances came to be regarded as identical with natural humus substances; the various representatives of humus substances were thought to be chemically individual compounds that could be isolated in a pure form, identified and given a formula and name.

Investigations on the chemical properties of humus substances—natural forms isolated from soils and peats, and artificial forms obtained by treating carbohydrates and other organic compounds with strong acids—were carried out by Berzelius's pupil, Mulder (1840, 1841, 1861, 1862). On the basis of numerous works of his own and of other investigators, which he incorporated in the book *The Chemistry of the Cultivated Layer*, Mulder classified humus substances according to colour and solubility in water and alkali solutions into the following groups: (1) those insoluble in alkali—ulmin and humin; (2) those soluble in alkali—ulmic acid (brown) and humic acid (black); (3) those soluble in water—crenic and apocrenic acids.

It should be mentioned that Mulder considered that, besides humus substances, various products of the decomposition of organic residues such as leucine, butyric acid, valeric acid and volatile compounds—formic acid and acetic acid, etc.—may also occur in the soil. Although he recognized their insignificant amounts and brief existence, Mulder thought, nevertheless, that they influenced plant growth in some way. The attention of Mulder and his contemporaries was, however, directed mainly to the study of humus substances.

In accordance with the views of that period, Mulder approached the study of humus substances on the assumption that they were chemically individual compounds and he attempted to free them in every known way from contaminants, one of which he believed was nitrogen. After the humus substances had been “purified” from contaminants and dried at 140° C to remove absorbed water (a procedure which no doubt altered the nature of the substances), Mulder determined their elementary composition, and on the basis of the experimental data he calculated their empirical formulae:

Ulmin	$C_{40}H_{32}O_{11}$
Humin	$C_{40}H_{30}O_{15}$
Ulmic acid	$C_{40}H_{28}O_{12}$
Humic acid	$C_{40}H_{24}O_{12}$ (or $C_{40}H_{30}O_{15}$)
Crenic acid	$C_{40}H_{24}O_{16}$
Apocrenic acid	$C_{24}H_{12}O_{12}$

Thus, although Mulder's works were undoubtedly important in the development of investigations on the chemical nature of humus substances and in the preciseness of their classification, they embodied the incorrect idea that humus substances were chemically individual compounds. At

that time, however, a new conception of humus substances arose which was more in correspondence with contemporary views.

The first serious challenge to the idea that humic acids were chemically individual compounds was made by the Russian investigator, German (1836, 1837, 1841, 1842, 1845). German's investigations were the outcome of a "production order" received from Prince Gagarin, a member of the landed aristocracy, who commissioned him to explain the cause of the decrease in the fertility of chernozems in spite of the fact that a large amount of humus still remained in them. German was also confronted with the task of explaining why the lost fertility of chernozem was restored under fallow.

Like many of his contemporaries, German (1836, 1837) believed that humus was a direct source of plant nutrients, and so he directed his main attention to its study. He found that cultivated soils contained less humus than did virgin soil and that in the composition of the humus there was a smaller amount of humic acid and a larger amount of crenic acid.

In accordance with these observations, German attempted to obtain scientific confirmation of the necessity of sowing root crops and fodder grasses but he expressed doubts as to whether the introduction of many-course rotations and the sowing of perennial grasses were possible in the near future (under the conditions of Tsarist Russia).

After isolating humus substances from various soils and peats and investigating artificial humus substances, German described 16 different representatives of the latter differing to some degree in elementary composition. He classified these substances into three groups, which in the main corresponded to those of Berzelius and Mulder (humic and ulmic acids, crenic and apocrenic acids, humin and ulmin).

Since German had no information on the structure and nature of humus substances (this became the subject of later investigations) and relied entirely on data on their elementary composition, he considered, in accordance with the ideas of the period, that each of the humus substances isolated by him was a chemically individual compound and to each of them he gave a special name and formula.

This was the fundamental error in German's work, although in principle his results indicating the diversity of both crenic and apocrenic acids and humic acids are correct and agree with present-day views according to which they are both regarded as group conceptions. His results indicating the occurrence in nature of many types of humus substance were criticized by Mulder, who thought that his conclusions were based on incorrect chemical data. This, however, was denied by German (1845).

Later, Odén (1919) ironically called German a “manufacturer of species” of humus substances, but German’s conception of the diversity of these substances was more in agreement with present-day ideas than were the views of Odén, who regarded humic and hymatomelanic acids as chemically individual compounds possessing definite properties.

Mulder’s strong criticism prompted German to offer an explanation of the origin of nitrogen in humus substances. German’s conception of the origin of nitrogen in humus by absorption from the atmosphere by rotting plant residues is, of course, naïve. His works are also not without methodological faults: the humus substances were extracted from peats and soils with ammonia solution, which increased their nitrogen content. German’s conception of nitrogen as a constituent part of the molecule of humus substance and not as a contaminant was, however, highly important in establishing the nature and origin of these substances: the presence of nitrogen indicates the complex character of the process of humus formation and the participation of nitrogen-containing compounds in the formation of humus substances.

Gradually, the number of isolated humus substances increased. Each investigator repeated the mistake of his predecessors by regarding the substance isolated as a chemically individual compound of specific chemical nature and by providing it with a formula and name. Thus, there appeared the “mucic acid” of Johnston, the “fumic acid” of Thenard, the “lignoic acid” of Hesse and, a little later, the hymatomelanic acid of Hoppe-Seyler (1889) among others. This resulted in a confused conception of humus.

Thus ended the second period of soil-humus investigations, whose course was influenced mainly by the development of chemistry. This period was characterized by the appearance of extensive works establishing the foundations of the study of the chemical nature of humus, the isolation of new representatives of humus substances (crenic and apocrenic acids) and the development of classification schemes. However, it was also characterized by the emergence of some incorrect ideas which had a retarding effect on subsequent humus studies.

One misconception—that humus substances were chemically individual compounds—arose from the absence of detailed investigations on their nature, structure and properties, which would have permitted a correct judgement of their genetic relationships or main differences. As a result of this misconception various humus substances for whose independent existence there was no justification were “invented”. This brought confusion into views on the nature of humus.

Incorrect also was the use of chemical methods to reproduce the

humification of plant material chemically (by treatment of carbohydrates, proteins, etc. with acids and alkalis); this was the result of insufficient knowledge of the biological basis of humus formation and of the leading role of micro-organisms in this process.

These mistakes inevitably influenced the further development of investigations on soil humus. Some investigators became sceptical of the actual existence of humus substances. This led to the development of incorrect ideas that soil humus was an indeterminate mixture of organic compounds of non-specific nature.

THE SECOND HALF OF THE 19TH CENTURY

A review of ideas on humus substances as natural compounds. The emergence of a new (biological) trend in the study of soil humus

The presence of an increasing number of humus substances whose independent existence was not confirmed by corresponding investigations, and the resulting confusion in terminology, produced doubts as to the existence in the soil of humus substances as a separate group of organic compounds of specific nature. The fact that the only means of isolating humus substances from the soil at that time was by alkali extractions, usually carried out with heating, contributed to these doubts. This treatment inevitably produced changes in the nature of the humus substances, and this fact, by analogy with the production of artificial humus-like substances from carbohydrates and other compounds, suggested that humus substances might be artificial products formed from plant material during their isolation from soils, peats and other natural materials.

There was also a critical attitude towards humic and ulmic acids, which appeared in the works of Eggerts (1889) and several other authors. Equally hypothetical, in Eggerts's opinion, was the existence of humus coals, which could not be isolated from the soil free from contaminants, and so their nature could not be studied. Only crenic and apocrenic acids were recognized by Eggerts as natural products since only they could be isolated in the form of aqueous solutions.

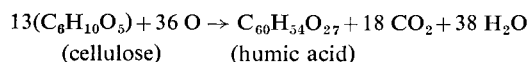
In the last decade of the 19th century studies on the colloidal-chemical properties of humus substances were begun; this was associated with the development during that period of colloidal chemistry. However, the results of these investigations not only failed to contribute to the precision of ideas on the nature of humus substances, but being misconstrued, they even served as further evidence against the existence of humus substances.

From the investigations of Tarkhov (1881) and Van Bemmelen (1888) it was plain that even if humic acid formed mineral salts this reaction was more complex than would be expected from stoichiometric laws and that it was masked by the formation of absorption compounds. After indicating the complexity of the composition of humus substances and the failure to isolate them as chemically individual compounds, Van Bemmelen concluded that crenic acid, apocrenic acid, ulmic acid, humic acid and also humin and ulmin were not homogeneous substances and the formulae used to represent them had no real significance; these substances were in fact amorphous and colloidal.

The results of Van Bemmelen's works were misinterpreted by some investigators. In a critical review of existing knowledge on humus substances, Baumann (1909) regarded them as complex mixtures of plant and animal residues in various stages of decomposition and difficult to separate from one another. Baumann and Gully (1910), on the basis of Van Bemmelen's results, assumed that the acid properties of humus were not due to the presence of compounds with functional groups but to its colloidal properties. Accordingly, the so-called salts of humic acids were really only absorption compounds.

Consequently, ideas on the nature of humus which arose from studies of its chemical nature and physico-chemical properties became increasingly complex. The problem of the origin of humus substances continued to be studied from a chemical standpoint; the artificial production of humus substances from organic compounds (mainly from carbohydrates) by treatment with acids also continued (Sestini, 1880; Berthelot and André, 1891–1892, 1896). Accurate investigations of these artificial preparations showed that there were large variations in their elementary composition depending entirely on the experimental conditions. These investigations, however, provided no answer to the problem of the mechanism of the process of humus formation.

The process of humus formation continued to be regarded as the oxidation and dehydration of plant materials. Thus, Detmer (1871) believed that humic acid originated from cellulose as follows:



On this basis, Detmer, like most of his predecessors and contemporaries, regarded humic acids as nitrogen-free compounds, but his attempts to free them from nitrogen were unsuccessful.

The role of humus in the soil remained obscure. Being opposed to the

idea that humus was a direct source of plant nutrients, Liebig (1840) rejected the humus theory of plant nutrition, stating that a high humus content of the soil is not the cause but the result of high yields. In Liebig's view humus is primarily a source of carbon dioxide, which is formed during its decomposition, and which promotes the solubility of inorganic soil compounds essential for plant nutrition. Some of the carbon dioxide on entering the atmosphere is assimilated by plants. This idea limiting the role of humus in the soil was, however, not in complete agreement with the views of other investigators.

Grandeau (1872) presented a new theory of organo-mineral plant nutrition in which humus substances were said to act as special "agents" between plants and the soil, promoting the conversion of insoluble and difficultly soluble inorganic compounds into available forms. This theory reconciled ideas on the mineral nutrition of plants with those on humus nutrition and at the same time indicated the newly discovered properties of humus substances—their participation in absorption and exchange reactions in the soil.

Into this atmosphere of contradictory and obscure views there was an influx of new ideas on the nature and origin of humus substances and their role in the soil. The brilliant investigations of Pasteur established the science of the biochemistry of microbes. Following his remarkable discoveries, Von Post (1862), Darwin (1882), Kostychev (1886, 1889), Müller (1887), Ramann (1888) and others established the important fact that humus formation is not a chemical or physical process but a biological one, resulting from the diverse activities of micro-organisms, protozoa and various other soil organisms (shrews, worms, insects).

In accordance with these discoveries, a series of investigations was started in which the decomposition processes of organic substances in the soil were studied biologically as well as biochemically, and the influence of various physical factors such as temperature, moisture and aeration on the intensity of these processes was explained. Into this category can be placed the classical works of Schloesing (1876, 1902), Kostychev (1886, 1889, 1890), Wollny (1886, 1897), Dehérain (1888), Dehérain and Demoussy (1896) and others. These works showed conclusively that humus is a source of nutrients (primarily nitrogen) for the plant, being converted into available forms during decomposition. They also showed the role of humus in the formation of soil structure and in providing the most favourable air and water regimes.

The emergence of this new biological trend in soil-humus study was all the more important because during this period Dokuchaev and Kos-

tȳchev laid the foundations of soil science in which soil was recognized as a natural body formed through the combined action of natural factors, particularly biological factors of soil formation such as the vegetative cover and the activity of living organisms. Humus was thus regarded as a most important soil constituent of great significance in soil-forming processes and in soil fertility; its presence in the soil was the qualitative feature distinguishing soil from the parent rock.

Dokuchaev and Kostȳchev's investigations were centred primarily on the problem of the origin of chernozem; this was of great scientific interest and productive importance in connexion with the restoration of soil fertility and in controlling severe drought. Dokuchaev's work *The Russian Chernozem* (1883) and Kostȳchev's *Soils of the Chernozem Region of Russia* (1886) were of such importance historically as to constitute a new era in soil-humus study.

By a detailed and comprehensive study of the distribution of chernozems in Russia, Dokuchaev was able to record geographical regularities in humus formation, which he represented by means of iso-humus belts. By extensive observations in natural environments, Dokuchaev and Kostȳchev established the exceptional role in chernozem formation of the biological factor — perennial grass vegetation, the roots of which, on dying-off every year, are a source of humus in the soil.

Dokuchaev and Kostȳchev showed that continuous cultivation of cereals on chernozem over a long period resulted in a decrease in soil fertility and increased the susceptibility to drought. Of particular importance were Kostȳchev's classical investigations on the humification of plant residues and his explanation of the role of micro-organisms and animals in the process. He investigated a number of problems on the effect of temperature, aeration and the physio-chemical properties of the soil on the decomposition rate of organic matter. All these investigations were carried out in attempting to discover the causes of the accumulation of humus in chernozems.

Kostȳchev showed the existence of a direct relationship between the accumulation of humus under perennial grasses and the physical properties of the soil, which favoured the retention of moisture. These investigations were highly important in connexion with the control of drought, which affected cultivated soils particularly severely.

These ideas of Dokuchaev and Kostȳchev were developed in the numerous works of their pupils and followers. Included in this category are the works of Sibirtsev (1900–1901), who was the first to show the role of crenic and apocrenic acids in the podzol-forming process, and the works

of Barakov (1886), Levakovskii (1888), Slezkin (1900), Naletov (1900) and Kravkov (1908, 1911), who studied the interaction between humus substances and the mineral part of the soil. Dokuchaev and Kostȳchev's teachings provide an inexhaustible source for further investigations even at the present day.

The new trend in soil-humus study, which was the result of the development of two disciplines, microbiology and pedology, occupied a prominent place towards the end of the last century. With the development of soil science the study of humus became wider, more profound and more definite; with the development of microbiology studies on the complex of problems of humus formation were put on a correct basis. At that time, however, microbiology offered no decisive contribution to the study of these problems.

In the last two decades of the 19th century, numerous investigations on the decomposition of plant substances and their role in humus formation were carried out. In accordance with the new ideas on the biological basis of the process of humus formation (as distinct from the artificial reproduction of this process by the treatment of plant materials with acids or alkalis) experiments were carried out under conditions which favoured normal biological activity.

These investigations were open to criticism, however, because they were carried out with *isolated* plant materials. Some works on the decomposition of plant materials were of very great interest; such were the works of Hoppe-Seyler (1889), who studied the biochemistry of the decomposition process of certain organic substances, Omelyanskii (1899, 1902), who studied the biochemistry of the anaerobic decomposition of cellulose, and also the investigations of Van Iterson (1904) on the aerobic decomposition of cellulose. These carefully conducted investigations gave no definite indication of the role of cellulose in the formation of humus substances because they were carried out with isolated cellulose.

The works of Snyder (1898), Suzuki (1906–1908) and those of investigators who studied the humification of isolated carbohydrates, oils, proteins, etc. are open to similar criticism.

At that time, the idea first originated that humus substances were complex compounds of *synthetic* nature and that their formation was the result of two reciprocal processes, *decomposition—synthesis*, involving the participation of two and perhaps more plant materials.

The first investigator to demonstrate the participation of products synthesized by bacteria in the formation of humus substances was Kostȳchev (1886). Then Hébert (1892) and Dehérain (1902) presented the

hypothesis that the formation of humus substances was due to a synthesis between proteins and encrusting substances (lignin). Later, this view was developed by Waksman (1938) in his theory on the "ligno-protein complex" as a nucleus of humus.

However, these views that humus substances are complex products of synthetic nature and that micro-organisms participate in their synthesis were not developed prior to the 20th century. At the turn of the century many investigators believed that humus was a complex and indeterminate mixture of organic substances of non-specific nature which are products of the decomposition of plant residues.

As has already been pointed out, this incorrect view was shared by some chemists whose sceptical attitude towards the existence of humus substances resulted from a number of methodological errors in their investigations.

THE FIRST TWO DECADES OF THE 20TH CENTURY

Further contradictions in views on the nature of humus. The accumulation of new facts on the origin of humus substances and the role of micro-organisms in their formation

The main divergences in views on the nature of soil humus arose during this period. Some investigators recognized humus substances as a group of compounds of specific nature and persistently continued the study of their properties, origin and formation mechanism. Others regarded soil humus as a complex mixture of organic substances representing decomposition products of residues of plant and animal origin; they regarded humus substances as artificial products formed during the extraction of the soil with alkali. Because of these views, investigators turned their attention to the isolation of various organic substances of non-specific nature.

The works of Schreiner and Shorey and co-workers (1908–1930) supported the latter ideas on soil humus. Using special apparatus by means of which they were able to extract organic substances from soil on a fairly large scale, followed by their fractionation and purification, these investigators established the existence of over 40 different chemically individual compounds belonging to various groups of organic chemistry: hydrocarbons, sterols, fats, organic acids, aldehydes, carbohydrates, organic phosphorus compounds and nitrogen-containing substances.

These investigations, carried out with great thoroughness and satisfying the strictest requirements of organic chemistry as regards the identification and chemical characteristics of the isolated substances, were

undoubtedly of positive importance in extending ideas on the substances of non-specific nature which are constituents of humus. In the works of earlier periods (for instance, in Berzelius's and Mulder's works), reference was made to the presence of this group of substances in humus, but the latter was insufficiently studied because attention was focussed almost entirely on the group of strictly humus substances.

In judging the importance of Schreiner and Shorey's works in the general development of humus teaching, it must be admitted that they also had a retarding effect by diverting the attention of most investigators at that time from a study of the strictly humus substances, which form a large part of the organic reserve of mature soils. A short but detailed review of Schreiner and Shorey's works was given by Shmuk (1924), who pointed out that these authors tried to divide the whole of humus into small groups and overlooked one important consideration – the specific reserve of organic substances in the soil.

It should be added here that Schreiner and Shorey carried out the isolation of the organic substances mainly from the acid filtrate obtained after precipitation of the humic acid, and also from the alcohol extract obtained after treatment of the raw humic-acid precipitate with alcohol. Moreover, the soil from which the organic substances were extracted had a low humus content and contained only a small amount of humic acids, which is not typical of the majority of soils.

However, at that time (beginning of the present century), in the presence of contradictory views and vagueness in ideas on the nature of humus substances, Schreiner and Shorey's investigations attracted general attention because of their precise nature. Attempts were also made to use the principles of their work for characterizing the nature of soil humus, which, however, did not give the expected results. Thus Khainskii (1916) could find no clear differences in the composition of the humus in genetically different soils (chernozem, podzol, chestnut soil).

Meanwhile, the study of humus substances as a group of complex compounds of specific nature was continued during this period by other investigators. Among the more important works in this direction were those of Odén (1912, 1914, 1919).

Odén thought that humus substances (he studied those of peats and to a less extent those of soils) could be divided into the following groups: humus coal, humic acid, hyatomelanic acid and fulvic acids (Table 1).

Humus coal corresponds to Sprengel's humus coal or to Berzelius's and Mulder's later definitions of humin and ulmin; it is insoluble in water, alcohol and alkali and only becomes partially soluble during fusion with alkalis.

TABLE 1. THE CLASSIFICATION OF HUMUS SUBSTANCES (after Odén)

Name of group	Behaviour towards			Salts and their properties	Colour	Characteristics
	Water	Alcohol	Alkali			
Humus coal	Insoluble and indispensible	Insoluble	Insoluble but liable to swelling	Little-known adsorption complexes	Black	Converted into humic-acid salts during alkali fusion
Humic acid	Sparingly soluble but disperses to form suspensions	Insoluble but partially disperses	Soluble	Alkali salts soluble in water and dispersing in alcohol. The remaining salts sparingly soluble but dispersing in water	Dark-brown with a reddish tinge	Equivalent weight 340. Contains carbon
Hymato-melanic acid	Sparingly soluble but disperses readily with the formation of suspensions and colloidal solutions	Forms true solutions	Soluble		Brown with a yellow tinge	Equivalent weight 250. Contains 62% carbon
Fulvic acid	Forms true readily diffusible solutions	Forms true solutions	Soluble	The majority soluble in water	Golden to pale yellow	Contains 55% carbon

Fulvic acids pass into solution, forming readily diffusible true solutions yellow to yellow-brown in colour, on the treatment of peat with water. In nature, these substances are found in marshy waters contaminated with colloidal substances. When these waters are subjected to ultrafiltration

solutions of a light-yellow to golden-yellow colour are obtained; concentrated solutions have an orange-yellow colour like that of potassium dichromate. Some of these substances are sensitive to oxidation (crenic acids), others are resistant (apocrenic acids). Recognizing that these substances were similar to Berzelius's crenic and apocrenic acids, Odén combined them into the group of "fulvic acids". He also noted that they had been insufficiently investigated and that the data on them from earlier literature were contradictory. The majority of the salts of fulvic acids are soluble in water and characterized by a relatively low carbon content ($< 55\%$).

In Odén's opinion, humus coal and fulvic acids were both group conceptions. The other two types of humus substances—humic acid (which he termed "humus acid") and hymatomelanic acid—were regarded as chemically individual compounds possessing certain constant characteristics.

Humic acid is dark-brown, almost black in colour, insoluble in alcohol but soluble in alkali; the equivalent weight is 340 and the carbon content 58 per cent. Hymatomelanic acid (a term introduced by Hoppe-Seyler) was, in Odén's opinion, identical with the previously described ulmic acid and is formed when humic acid is decomposed during its extraction with alkali solution. Hymatomelanic acid has a lighter colour than humic acid (chocolate-brown), is soluble in alcohol, has a lower equivalent weight (250) and a carbon content of 62 per cent.

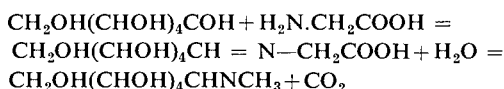
The results of Odén's investigations on the colloidal-chemical properties of humus substances are of particular interest. Using the potentiometric titration method, he demonstrated that hydrogen ions were present in humic acid at a concentration corresponding to pH 3.87. In determining the electrical conductivity of humic acid neutralized with NaOH, Odén found that it was tri-basic although he later described it as a tetra-basic acid. The results of his studies on humic-acid soils, his ultramicroscopic investigations, etc., deserve special attention. The data of his investigations on the physico-chemical properties of humus substances confirmed the necessity for liming on acid peat soils.

In judging the importance of Odén's works in the development of general ideas on the nature of humus substances it must be mentioned that some of his arguments cannot be regarded as correct. A case in point is the conception of "fulvic acids", which he considers, in the absence of sufficient evidence, to be analogous to Berzelius's crenic and apocrenic acids. Moreover, his conclusion that hymatomelanic and ulmic acid are identical was without foundation. His principle of separating humus substances according to their behaviour towards solvents (particularly to water) was only provisional, as many investigators have since shown.

During the same period renewed attempts were made to explain the most important problems of soil humus concerning the origin of humus substances, the mechanism of their formation and the role of micro-organisms in this process. No definite conclusions were reached on these problems although the observations of some investigators may be regarded as having provided the correct basis for their solution. The idea that humus substances were products of a synthesis became more and more certain. There was no longer any doubt about the presence of nitrogen in humic acids; the results of the investigations of Doyarenko (1901), Suzuki (1906–1908), Jodidi (1910–1913), Kelley (1914) and others had revealed the protein nature of the nitrogenous fraction of humic acids. Furthermore, the aromatic nature of humic acids was established in other investigations. Sestini (1902) confirmed Hoppe-Seyler's previous observations (1889) that phenol derivatives are among the products obtained by subjecting humic acids from peat and brown coal to alkali fusion. The conclusion that humic acids were the condensation products of nitrogen-containing compounds with aromatic substances of the polyphenol type was not made until much later.

Maillard (1912–1917) attempted to synthesize humus substances by means of a reaction between amino-acids and carbohydrates and succeeded in obtaining dark-coloured humus-like substances of the melanin type even with slight heating.

He represented the reaction as follows:



In Maillard's opinion, condensation was a purely chemical process and the role of micro-organisms in humus formation was limited solely to the first stage—the hydrolysis of proteins to peptides and amino-acids and the hydrolysis of polysaccharides to simple sugars.

These experiments, of course, were carried out in conditions far removed from those in nature, for, as is well known, carbohydrates are decomposed extremely rapidly by micro-organisms with the formation of low-molecular-weight acids and products of complete mineralization and, therefore, could hardly serve as the initial substances of a synthesis. However, Maillard's idea that humus substances were products synthesized from simpler substances formed during the decomposition of the original plant residues was, in fact, correct.

In the meantime, a great mass of data had accumulated showing that plant residues undergo complex biochemical transformations during

humification. Thus, Beijerinck (1900) established that an actinomycete (*Streptothrix chromogenus*) produced aromatic compounds of quinone type in a medium containing peptone. Perrier (1913) found that, under aerobic conditions, salts of benzoic and salicylic acids were converted into dark-coloured condensation products as a result of the action of fungi and bacteria (*Bact. pyocyaneum*). Naturally, the idea developed that oxidation and condensation processes were in some way connected with the enzymic activity of micro-organisms. Of great interest are Bertrand's investigations (1898), which demonstrated that the oxidation of tyrosine and certain polyphenols (gallic acid, pyrogallol, guaiacol and some others) by oxidases converted these substances into dark-coloured condensation products.

Of the investigations of this period, particular attention should be paid to those of Trusov on the origin of humus substances and the mechanism of humus formation. Although these investigations were not completed because of Trusov's untimely death, they nevertheless contain many extremely valuable ideas.

Trusov, one of Kravkov's talented pupils, devoted many years of his life to a systematic study of the process of humus formation. His first works (1914) were not free from the methodological errors characteristic of the earlier periods. For instance, in investigating the sources of humus substances, Trusov began by producing humus-like substances by subjecting plant materials (proteins, simple sugars, cellulose, plant oils, tannic substances, etc.) to treatment with strong acids. Later, however (1915), he turned his attention to experiments on the humification of plant materials—in isolated form or in artificial mixtures—under conditions which allowed normal biological activity to proceed. Subsequently (1916), he studied the origin of humus substances with plant residues—leaves of woody species and grass vegetation.

On the basis of his experiments, Trusov concluded that different plant materials could serve as the source of humus. At the same time, compounds readily utilized by micro-organisms (cellulose, hemicelluloses, mono- and disaccharides, glucosides, organic acids, etc.) are indirect sources of humus substances, being converted first into microbial plasma, which then participates in the formation of humus substances.

The other part of the plant residues, represented by plant material not readily utilized by micro-organisms (mainly of aromatic nature—lignin, tannic substances, amino-acids of aromatic structure), is a direct source of humus substances. The course of humification of these substances is generally similar and Trusov indicated it by the following sequence: (1) hydrolytic decomposition with the formation of simpler substances of

aromatic nature; (2) oxidation of the latter with the formation of quinones (Trusov's "hydroxy-quinones"); (3) further condensation of the quinones and their conversion into dark-coloured complex products (humic substances).

In Trusov's opinion, the alkaline reaction produced by ammonia formed during the decomposition of proteins by micro-organisms promotes the oxidation of aromatic compounds. However, in his later works, Trusov indicates the great role of the oxidizing enzymes (oxidases) of decomposing plant tissues, as well as those of micro-organisms, in this reaction which is so important in humus formation.

Trusov showed the possibility of the participation in humus formation of various plant materials which undergo complex biochemical transformations during humification. In some cases the transformation of the original materials into humus substances proceeds through microbial plasma. Thus, Kostychev's idea of the participation of products of microbial synthesis in the formation of humus substances found re-expression in Trusov's works.

Of great interest are Trusov's ideas that aromatic compounds can be converted into humus substances by means of their oxidation to quinones by enzymes of micro-organisms, followed by condensation of the quinones with the formation of complex, dark-coloured products. These views of Trusov, based on general ideas on the oxidation and condensation of aromatic compounds, have been confirmed in the works of recent authors (see Chapter 3).

In Trusov's works there were no investigations on the chemical nature of the humus substances whose formation he observed in his numerous experiments. In our opinion this is not accidental, but is explained by Trusov's scepticism towards the existence of humus substances as a group of compounds of specific nature; he regarded them as complexes of various compounds.

A detailed study of the nature, structure and properties of humus substances was made by Shmuk, Trusov's contemporary. The works of these investigators can be regarded as complementary. While Trusov's main interest was in the origin and biochemistry of the formation of humus substances, Shmuk was primarily concerned with their chemical nature, structure and physico-chemical properties. In his final work (1930) Shmuk reviewed the more important general theoretical aspects of the soil-humus problem and presented his views on the origin of humus and the role of micro-organisms in its formation.

Shmuk (1924) expressed clearly his attitude towards Schreiner and

Shorey's works and also his views on the nature of humus substances. In his criticism of the American investigators, Shmuk pointed out that with the diversity of the plant and animal residues entering the soil and with the varied nature of the microbiological activity one would naturally expect in soil, which is a complex medium, the presence of larger or smaller amounts of all the substances occurring in plants and animals and produced by micro-organisms—from carbonic acid to complex proteins.

However, the substances isolated by Schreiner and Shorey and their co-workers are present in the soil in amounts not exceeding a few tenths of a mg per many tens of kg of soil and their occurrence is far from constant being dependent on the crop residue added. The majority of these substances are not related to the total content of organic matter nor to any other specific characteristics of the soil.

Shmuk regarded humic acids as the most characteristic constituents of humus and had no doubts about their specific nature. Nevertheless, he tended to think of humic acids not as chemically individual compounds but as a *group* of compounds with general structural features.

Shmuk showed that Odén's scheme of dividing humus substances into groups according to their solubility in different solvents is provisional. Thus, from humic acid (from chernozem) in a moist state, Shmuk isolated two fractions: one fraction soluble in hot water (1/3 of the total) and the other fraction, insoluble in water, representing the remainder. If the moist humic acid is first dried at 100°, then made into a powder, it completely loses its capacity for dissolving in water. It will be remembered that a similar phenomenon was described by Sprengel. In this case, therefore, we are dealing not with different chemical substances, but with one and the same substance occurring in a different physical state.

On the basis of many investigations and data from the literature, Shmuk put forward the idea that humic acids are highly dispersed suspensions occupying a position intermediate between colloids and crystalloids, yet possessing, at the same time, a number of characteristics typical of substances in the colloidal state—the capacity for precipitating with electrolytes, adsorption properties, swelling, etc.

Shmuk's investigations contributed greatly to ideas on the chemical nature and structure of humic acids. By esterifying a humic acid from chernozem with alcohol in the presence of dry hydrogen chloride Shmuk showed that ethyl esters were formed, thus indicating the presence of the carboxyl group in the humic acid. By treatment with benzoyl chloride he obtained esters of benzoic acid, thus indicating the presence also of hydroxyl (phenolic) groups in humic acid.

An extremely important part of Shmuk's work was his study of the forms in which nitrogen occurs in the soil. He regarded nitrogen as a constituent of humic acids (in this respect his ideas differed from those of Odén, who regarded nitrogen as a contaminant of humic acid). In his early work (1914), Shmuk had already shown that the nitrogen of various soils (chernozem, podzol, krasnozem) was probably of protein origin, since the ratio of mono- to diamino-acids in soil nitrogen corresponds to that found in proteins of plant and animal origin. Later (1924), he found that this was true also for humic acids from chernozem; this was confirmed by the data of Doyarenko, Jodidi and others. On the assumption that nitrogen-containing organic compounds of plant residues are decomposed very rapidly by micro-organisms, Shmuk considered that soil nitrogen as a whole, and the nitrogen of humic acids in particular, was of secondary origin, its source being the plasma of micro-organisms.

In Shmuk's work, as in Trusov's, there was a development of Kostychev's idea of the participation of a secondarily synthesized organic substance (a constituent of microbial plasma) in the formation of humus substances.

Shmuk (1924) was the first to establish the aromatic nature of soil humic acids, although Hoppe-Seyler (1889) had already shown this to be true for humic acids isolated from peat and brown coal. Shmuk, retaining Hoppe-Seyler's methods (fusion with concentrated KOH at 245° C), found aromatic products of protein decomposition (indole, skatole, pyrrole, protocatechuic acid) in the fusion products of humic acid from chernozem. From the evidence that no appreciable amounts of phenol derivatives were formed from aromatic amino-acids (tryptophan, tyrosine, phenylalanine) or from certain organic compounds of the fatty series during alkali fusion, Shmuk believed that the composition of the fusion products indicated the presence in humic acids of the benzene ring.

Thus, Shmuk concluded that 2 components were present in the humic-acid molecule: an organic nitrogen-containing compound (of microbial origin) and the benzene ring. Shmuk believed that these two components occurred in chemical linkage with each other and not in the form of a simple mixture. However, he did not disclose the nature of this linkage.

Moreover, Shmuk's ideas on the structure of humic acid, in conjunction with Trusov's ideas on the mechanism of the conversion of aromatic compounds into humus substances through oxidation (by enzymes) to quinone and subsequent condensation and self-condensation of the latter, have led to the present-day theory that humic acids are products of the condensation of an aromatic compound (oxidized biochemically to quinone) with a nitrogen-containing compound of protein origin.

Shmuk's works, however, are not without some faults. After establishing the presence in the humic-acid molecule of the aromatic ring, he formed the opinion that lignin was its main source. After pointing out the genetic relationship between humic acids, lignin of plant residues and proteins of microbial origin, Shmuk stated that "only by combining the lignin theory with the idea of a plasma protein and its transformation in the soil, can a satisfactory theory on the origin of soil humus be worked out" (1930, p. 77).

These views that lignin is one of the two main sources of humic acids were greatly influenced by the lignin theory on the origin of humic acids that predominated at that time. However, the aromatic ring of humic acids can doubtless originate from other sources besides lignin, such as tannic substances, polyphenols (respiratory catalysts), and also polyphenols of secondary origin formed from substances of non-aromatic nature as a result of microbial activity. Shmuk's views on the nature of some groups of humus substances do not conform with contemporary views. For instance, he considered the fraction of humus insoluble in alkali (humin) and also crenic and apocrenic acids to be an unstable mixture of plant residues occurring in various stages of humification.

However, judging from the value of their works, those brilliant investigators, Shmuk and Trusov, should be included among the group of scientists who have contributed greatly to the study of soil humus.

We shall conclude this survey of the works of the first twenty years of the 20th century by considering the main points in Williams's teaching on soil humus. This incorporated the progressive ideas of earlier periods, in particular, the ideas of Dokuchaev and Kostychev who founded the science of soil genetics.

Williams's teaching was the outcome of investigations over a long period. As early as 1902, in a lecture on "The Importance of Organic Matter in the Soil", read at the Annual Meeting of the Scientific Council of the Moscow Agricultural Institute (now the Timiryazev Agricultural Academy), Williams stated the principles of his teaching on biological associations, including plants and micro-organisms, which determine the direction of the soil-forming process, and also the character of the decomposition of organic residues and the nature of the humus substances formed.

Later, on the basis of these principles, Williams developed his teaching on plant associations, on their change, on the soil-forming process and on soil types as stages in this process. He presented his views on soil humus during a course of lectures on soil science (1897, 1914).

During the years of Soviet rule, Williams's teaching on soil humus, enriched with new data, formed the basis of his ley system of agriculture.

The underlying principle in all Williams's works was the idea that humus formation was a system of interrelated *biological* phenomena governed by the law of continuity of movement. Humus is the result of an equilibrium between reciprocally related processes: life→ death; symbiosis → antibiosis; the synthesis of organic substances in the living plant → their decomposition by micro-organisms after death → the synthesis of humus substances.

Williams presented a clear argument for the existence of two stages in the process of humus formation, the first stage being the decomposition of the original plant residues to simpler compounds, and the second stage, the synthesis of substances of complex nature (humic). Williams also postulated that both stages of humus formation—decomposition and synthesis—are the result of the enzymatic activity of micro-organisms.

Williams was critical of the use of drastic methods for isolating humus substances and gave as an example the works of the last century in which dark-coloured products were obtained from carbohydrates by treatment with concentrated solutions of acid and alkalis with heating. He stated “a black liquid such as this can be obtained from any organic material: flour, straw, sawdust, animal corpses” (1939, p. 65).

In order to obtain humus substances Williams carried out field experiments with lysimeters: dilute solutions of humus substances were extracted in the drainage water. There could be no doubt, therefore, about the natural occurrence of these substances.

After many years of persistent work, Williams came to the conclusion that humus substances were a group of organic compounds of specific nature similar to those described by Berzelius. He wrote: “According to Berzelius's investigations, generally confirmed by my work, the natural humus substances of the soil are represented by three acids. With regard to their names I prefer to retain the ones that were used in the historical development of the science—ulmic, humic, crenic... The properties of humic acids were already known to Berzelius and my works were merely supplementary” (1939, p. 73).

Thus, Williams's investigations on the humus substances from lysimeter waters are of great importance in solving a major problem—the *actual* existence of humus substances as natural products.

Dokuchaev's and Kostȃchev's ideas on the role of the vegetative cover, the importance of natural conditions for the formation and accumulation

of humus and the importance of humus in soil formation and soil fertility were developed in Williams's teaching.

The whole diversity of conditions under which the process of humus formation takes place is classed by Williams into three main types of biological association comprising green plants and organisms possessing no chlorophyll:

1. A biological association consisting mainly of woody vegetation and micro-organisms: fungi, actinomycetes and anaerobic bacteria. Williams attributes the podzolization of the upper layer of soil under forest to the action of crenic acids formed during the aerobic decomposition of woody vegetation by fungi.

2. The association consisting of meadow-grass vegetation and bacteria, mainly anaerobic forms but also including some aerobic forms. Under these conditions the branched root systems of the grasses give the soil a crumb structure. Ulmic acid formed during the anaerobic decomposition of the grass residues by bacteria saturates the soil crumbs and gives them stability. These features characterize the sod stage of soil formation. Williams made a reproduction of the meadow stage of association under agricultural conditions the basis of his ley system of agriculture.

3. The steppe association consisting of grass vegetation and aerobic bacteria. Under these conditions humic acids are formed; the latter are biologically unstable because of their conversion into ammonium salts which are rapidly utilized by micro-organisms. With the development of steppe vegetation, therefore, a more complete decomposition of organic substances and of soil humus is observed, which leads to a deterioration of soil structure.

According to Williams, the appearance in the medium (soil) of new characteristics leads to the development of new properties which result in a change in the association. This was the origin of Williams's teaching on the unique soil-forming process and the recognition of soil types as stages in this process.

Williams's ideas on biological associations and their change during soil formation still require constructive development by pedologists, biochemists and microbiologists.

Being closely connected with agriculture, Williams used his theoretical views on the origin and properties of humus and its participation in the nutrient regime of soil and in structure formation as a basis for developing measures for increasing soil fertility. Thus, his works are an example of the combination of theory with the most important problems of soil genetics and with the practical tasks of agriculture.

With this brief account of the basic ideas in Williams's works we shall conclude the survey of the principal works on soil humus of the first two decades of the 20th century.

It is clear from this survey that a range of problems concerning the nature of humus substances, their origin, the biochemistry of humus formation and the importance of humus in soil-forming processes and soil fertility occupied the attention of investigators during this period.

It is plain from these works that by the end of this period, in spite of a large number of conflicting opinions and the misconceptions and mistakes of some investigators, correct solutions to many of the problems were found and a correct lead given to investigations on a number of other problems. The works of the Russian investigators Trusov, Shmuk and Williams played an outstanding part and contributed greatly to the knowledge of soil humus during this period.

The most important general principles arising from the works of this period can be summarized as follows:

1. As a result of the more detailed study of the nature and properties of humus substances their existence in the soil as natural products was convincingly demonstrated.

2. It was established that various plant materials in the course of complex transformations of a biochemical character can serve as sources of humus substances. Kostychev's idea that products of bacterial synthesis were involved in the formation of humus substances was confirmed in many works.

3. Results of a study of the nature and structure of humus substances (humic acids) showed that they were the products of a two-stage process — the decomposition of the original plant materials to more simple compounds and the subsequent synthesis of complex humus substances. The view that humic acids were the products of a condensation of aromatic compounds with nitrogen-containing organic compounds was expressed.

4. It was suggested that the enzymatic activity of micro-organisms was involved, not only in the first stage of the process (decomposition), but also in the second stage (synthesis) in which oxidizing enzymes of micro-organisms participate actively.

It was natural, therefore, that further studies on soil humus should be directed towards the development of these ideas, their verification in nature and the utilization of the results obtained to solve the problems of soil genetics and to increase soil fertility. However, a false step was made during the next 10–15 years — the years directly preceding the contemporary period — which for a long time put investigators on the wrong track.

FURTHER INVESTIGATIONS DURING THE 20TH CENTURY

Investigations on the chemistry of humus of coal, brown coal and peat;
their application to the study of soil humus

During this period, investigations on the chemistry of the humus of coal, brown coal and peat, largely developed in Germany (Fischer and Schrader, 1921, 1922; Fuchs, 1931–1936; and others), had a fundamental influence on the study of soil humus. These investigations are undoubtedly of great interest as an example of a careful and detailed study of the nature and structure of humus substances; the methods used are also applicable to the study of soil humus substances (for instance, the determination of functional groups, the study of the decomposition products of humus substances during oxidation and during fusion, etc.).

Unfortunately, these works on the chemistry of the humus of coal and peat have been overrated and the views of the German chemists on the origin of humus substances and the mechanism of humus formation have been applied indiscriminately to soil-humus studies in spite of the fact that the natural conditions of peat and coal formation do not correspond with the conditions of humus formation in the soil.

As to the question of the origin of humus substances (humic acids), there were at this time two opposing views. Was their source the cellulose or the lignified tissues of plant residues? The opinion that cellulose was the source was expressed (for peat humic acids) by Marcusson (1922, 1925, 1926, 1927). He believed that cellulose undoubtedly participated in the formation of humic acids, being converted physico-chemically into oxy-celluloses. Uronic complexes, which are constituents of the latter, readily acquire, through furan derivatives, an aromatic structure and are converted into humic acids.

However, the most generally accepted views in the 1920's and '30's were those of Fischer and Schrader, and Fuchs. In their opinion the main source of humic acids was lignin, which, during humification, underwent a number of complex transformations, mainly of a physico-chemical character (oxidation, condensation, etc.). The important arguments in favour of this theory were:

1. A similarity in the nature of humic acids and lignins—the presence in the molecules of both substances of the aromatic ring and certain functional groups (methoxyl OCH_3 , phenolic hydroxyl OH).
2. The production of humus substances from lignin when it is subjected to alkaline oxidation in an autoclave (Fischer and Schrader's experiments,

1922). Under similar conditions Willstätter and Zechmeister (1913) obtained only weak-coloured, low-molecular-weight compounds from cellulose.

3. The relative resistance of lignin to microbial action and the rapid decomposition of the carbohydrate components (in particular, cellulose) to low-molecular-weight substances and products of complete mineralization.

Although we shall not deal here with less important arguments presented by followers of the lignin theory of the origin of humic acids in support of their views, it should be mentioned that a critical examination leaves certain doubts as to the correctness of certain aspects of the theory and even as to its validity as a whole.

The first argument, based on the presence of the aromatic ring in both lignin and humic acids, cannot be regarded as convincing because plants also contain aromatic substances of non-lignin origin; such are the tannic substances, polyphenols—respiratory catalysts, and, in rotting plant residues, aromatic compounds of secondary origin (products of microbial activity, constituents of microbial plasma).

The second argument, based on experiments on the oxidation of cellulose and lignin in an autoclave, is also rather unconvincing because the experimental conditions were artificial and differed completely from natural conditions.

There are also doubts as to the correctness of the third argument which was based on numerous comparative studies of the chemical composition of fresh and humified plant residues. These works (Wehmer, 1915, 1925, 1927; Rose and Lisse, 1917; Bray and Andrews, 1924; Grosskopf, 1926, 1928, 1929, 1935; and others) show clearly only that certain substances (e.g. sugars, cellulose, hemicelluloses, proteins) decompose more rapidly than lignin. But which plant substances participate in the formation of humus substances and the actual mechanism of the process remains obscure.

The lignin theory of humic-acid origin was very popular with the investigators of coal and peat (in the USSR the most ardent follower was Stadnikov) and also with investigators of soil humus; the theory was slightly modified for soil humus by Hobson and Page (1932) and by Waksman and co-workers (Waksman and Tenney, 1927, 1929, 1930; Waksman and Gerretsen, 1931; Waksman and Iyer, 1932–1933; Waksman and Stevens, 1930).

In numerous experiments with various plant residues Waksman, in general, established the same regularities in the decomposition of plant

materials as were found in the works quoted above: cellulose and simple carbohydrates are decomposed most intensively; the decrease in the amount of hemicelluloses and proteins is less marked, because side by side with the decomposition of the original hemicelluloses and proteins takes place their resynthesis in the form of plasma of micro-organisms, large numbers of which develop in humifying plant residues.

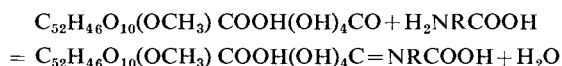
The material most resistant to decomposition is lignin, the content of which decreases only slightly compared with the decreases in the content of materials of other groups. To illustrate this, the data from one of Waksman's experiments are presented (Table 2).

TABLE 2. THE CHANGE IN CHEMICAL COMPOSITION OF RYE STRAW DURING DECOMPOSITION (Waksman, 1938)

Composition of straw	At beginning of decomposition	After decomposition for 2 months under aerobic conditions
Total organic matter	100.0	58.0
including:		
cellulose	41.5	18.3
pentosans	26.0	10.3
lignin	22.5	20.0
proteins	1.2	3.4

Summarizing the results of his investigations, Waksman concluded that readily decomposable substances (cellulose, simple carbohydrates, etc.) are of little importance in humus formation; the sources of humus substances are, firstly, the lignin of plant tissues and, secondly, the proteins resynthesized into microbial plasma.

In the interaction between these two components, as in Schiff's reaction, the humus nucleus —“ligno-protein complex”—is formed as follows:



Waksman's theories on humus composition, on the origin of humus substances and on the mechanism of humus formation were a reflection of Schreiner and Shorey's views on the one hand, and those of Fischer and Schrader and their followers—the investigators of the chemistry of coal and peat—on the other.

In accepting Schreiner and Shorey's ideas, Waksman denied the existence in the soil of humus substances as compounds of specific nature, and

regarded them as artificial products formed by the action of alkali solutions on the soil.

On this basis, he regarded humus as a mixture of substances of non-specific nature including cellulose, hemicelluloses, proteins, fats, waxes, simple carbohydrates and other compounds. Waksman's scepticism towards the specificity of natural humus substances was revealed too by the fact that, even in the case of a newly formed compound of synthetic nature, he retained the original name of the substance — "ligno-protein complex".

The following is a quotation from Waksman's book *Humus* (1938): "There is no doubt now that this complex originates mainly from the lignin constituents of plant residues, by various biological and chemical modifications; this fraction [humus substances—M. K.] may, therefore, be included in the lignin group."

During the 1920's and '30's, Waksman's views on the nature of humus, the origin of humus substances and the mechanism of humus formation were widely accepted. Attempts were made to use Waksman's method—the basis of which, in accordance with his views that humus was a mixture of plant materials, is the method of plant analysis—to expose genetic differences in soil humus.

In addition to this, data gradually accumulated which made a criticism of Waksman's ideas on soil humus essential.

Tyurin in his book *The Organic Matter of Soils* (1937) regards Waksman's denial of the existence in soil humus of strictly humus substances in addition to substances of non-specific nature as unfounded and incorrect. He showed the unsuitability of Waksman's method of determining the composition of soil humus, because when it was tested on genetically different soils, the differences in humus composition were found to be very small. This was also exposed in Waksman's own works (Waksman and Hutchings, 1936).

At that time, various other investigators were also critical of Waksman's views. The discussion between Waksman (1935) and Springer (1934–1935), in which Springer supported the existence of humus substances as compounds of specific nature, should be mentioned. Moreover, the individual points in Waksman's concept of humus were not confirmed. Thus, his assertion that the ligno-protein complex possessed a new property (compared with the original substance), viz. an increased capacity for exchange reactions, was found to be incorrect. It was shown (Lein, 1940) that this property was the result of treating lignin with alkali, a point which Waksman overlooked.

The view that lignin is the main source of humus substances has not

been confirmed. Many investigators have shown the possibility of a non-lignin origin of humus substances: during the heating of grain (Mishustin, 1938), during the early stages of humification of plant residues (Kononova, 1943, 1946), during the decomposition of microbial plasma (Sorokina and Tyagny-Ryadno, 1933; Rippel, 1931, 1935; Gel'tser, 1940; Tepper, 1949, 1952; Harmsen, 1951; and others).

The products of the activity and metabolism of various micro-organisms (mould fungi, actinomycetes and certain heterotrophic bacteria) are of considerable importance in the formation of humus substances. That they can form compounds of an aromatic or similar nature during the utilization of the original substances of aliphatic nature (including carbohydrates) was shown by many investigators (Raistrick *et al.*, 1933, 1940, 1941; Laatsch *et al.*, 1948, 1950, 1952; Scheffer, Plotho and Welte, 1950; Plotho, 1950, 1951; Flaig, 1950, 1952, 1958; Welte, 1952; Küster, 1952, 1955; Kononova and Aleksandrova, 1956, 1958; Mishustin, Dragunov and Pushkinskaya 1956; and others; see Chapter 3).

There is evidence, therefore, that many organic substances can participate in humus formation and that considerable changes occur during the course of their conversion into humus.

Moreover, the new data of English scientists (Bremner, 1955; Tinsley and Zin, 1954; Jenkinson, 1956; Jenkinson and Tinsley, 1960), investigating the nature of lignin and the forms of nitrogen occurring in the soil have raised doubts as to the correctness of the theory that the ligno-protein complex is the main constituent of soil humus.

THE PRESENT STAGE IN SOIL HUMUS STUDY

In post-war years, the soil-humus problem has continued to attract the active attention of investigators as evidenced by the existence of a large volume of literature. The scope of problems investigated has become more diverse and improvements have been made in the methods of investigation. Investigators in various branches of science—pedologists, chemists, microbiologists, zoologists, plant physiologists and agronomists—in a number of different countries (including England, Belgium, Bulgaria, Hungary, E. Germany, Holland, India, Poland, USSR, USA, Finland, France, W. Germany, Czechoslovakia, Sweden, Japan) are providing the solution to important theoretical and practical questions and there is ample justification at this stage for speaking of an advance in humus study.

As we shall be dealing later with current ideas on the nature and functions of soil humus, we shall limit ourselves here to a brief statement of

the main lines of investigation that are being followed at the present day. Many of the recent works deal with the nature of humus substances; the use, in conjunction with chemical methods, of methods such as X-ray analysis, electron microscopy, infra-red spectroscopy, chromatography, etc., has revealed certain characteristic features in their structure. The comparative study of their nature and composition in different soils makes it possible to establish regularities in humus formation depending on the complex of conditions in the soil medium, and is making the role of humus substances in soil-forming processes in different soils more precise.

Problems on the origin of humus substances and the mechanism of their formation have attracted no less attention. In these highly complex problems much progress has been made during recent years. Investigations from a biochemical standpoint have helped to show that the formation of humus substances is due to complex transformations of the original organic residues. In bringing this process about a great part is played by the enzymatic activity not only of micro-organisms but also of representatives of the animal kingdom.

Much new and valuable information has been incorporated into existing ideas on the role of organic matter in the weathering of parent rocks and minerals, in soil formation, on the nature of the interaction between organic matter and mineral compounds and on certain other questions.

The study of various problems closely connected with agriculture (the role of organic matter in the formation of soil structure, in the supply of carbon dioxide and nutrients to the plant, etc.) has revealed the extremely important fact that soil organic matter participates in the physiological processes of the plant and also in the biochemistry of its nutrition. The results of these investigations introduce new ideas into the theory of plant nutrition and there is no doubt about their importance for the development of correct methods of cultivation and for the efficient use of fertilizers. These aspects will be discussed in detail in the following chapters.

CHAPTER 2

CONTEMPORARY IDEAS ON THE COMPOSITION OF SOIL ORGANIC MATTER AND THE NATURE OF HUMUS SUBSTANCES

THE ORGANIC part of the soil consists of a complex system of substances, the dynamics of which is determined by the continuous admission of organic residues of plant and animal origin into the soil and their continual transformation under the action chiefly of biological factors, but also, to some extent, of chemical and physical factors. This explains the fact that in the organic part of the soil various substances are present which represent the components of organic residues undergoing decomposition, metabolic products of micro-organisms utilizing organic residues as a source of energy, products of secondary synthesis in the form of bacterial plasma and strictly humus substances. The whole diversity of soil organic compounds can be classified into two main groups.

The first group of substances (components of decomposing plant and animal residues, products of their decomposition and products of resynthesis in bacterial cells) consists of various nitrogenous and non-nitrogenous organic compounds belonging to well-known groups of organic chemistry, e.g. proteins and their decomposition products, carbohydrates, organic acids, fats, waxes, resins, etc. Collectively, these compounds of non-specific nature form 10–15 per cent of the total amount of soil organic matter.

There are also present in soils substances, which, because of the peculiarity of their nature, cannot be related to any of the existing groups of organic chemistry. The nature, origin and properties of these substances are not yet fully understood. However, because of the regularity of their isolation from soils, decomposing plant residues, peats and other natural formations, these substances are justifiably included in a separate group termed humus substances. In developed soils this second group forms a large part of the total reserve of organic matter—up to 85–90 per cent.

Substances of both groups, including fresh and incompletely decomposed organic residues from plants and animals make up “soil organic matter”. This concept is therefore wider than soil “humus”. It must be

remembered that “humus” includes not only strictly humus substances, but also products from the advanced decomposition of organic residues and also products resynthesized by micro-organisms (protein-like substances, carbohydrates, lignins, waxes, resins, fats, tannins, etc.) which remain in the soil sample during the preparation of the soil for determination of its “humus” content.

This can be illustrated by the following scheme.

Soil organic matter		
Humus		Fresh and incompletely decomposed plant and animal residues
Strictly humus substances; Groups: Humic acids Fulvic acids Humins Hymatomelanic acid	Products of advanced decomposition of organic residues and products resynthesized by micro-organisms (protein-like substances, carbohydrates, waxes, fats, tannins, lignins, etc.)	

We shall use the terminology of this scheme in all further discussion.

It is important to realize that authors often differ in the meanings they attach to the terms “humus”, “soil organic matter”, “humus substances”, “humus and humic acids”. Some research workers (e.g. Scheffer) rightly hold the opinion that the terminology of organic substances in the soil should be ordered and unified.

The great diversity of soil organic substances, present often in negligible amounts, their dynamic state and the difficulty of isolating them from the soil in unchanged form (particularly the fraction occurring in the form of organo-mineral compounds) have so far been serious obstacles to the study of soil organic matter. These difficulties can, however, be overcome.

Investigations carried out during recent years with the object of studying humus substances extracted from soils by relatively mild methods (using neutral solutions, low concentrations of alkali in the cold in a stream of inert gas) give a much broader view of existing ideas on the composition and nature of soil humus substances and reveal in the structure and properties of the individual representatives, certain specific features which depend on the conditions of soil formation.

The review of contemporary theories on the nature of soil humus is divided into two parts—in the first part are grouped organic substances of non-specific nature, and in the second part, substances characterized as the group of strictly humus substances.

ORGANIC SUBSTANCES OF INDIVIDUAL NATURE

In this extremely diverse group, which includes the constituents of decomposing plant residues, various products of microbial activity and products of resynthesis in the form of bacterial cells, one can expect the presence of substances related to the following groups of organic compounds:

1. Fats and similar substances.
2. Carbohydrates and related substances (mono- and disaccharides, cellulose, hemicelluloses and pectins, pentosans, mannans, polyuronides of plant and microbial origin).
3. Proteins and their derivatives, albumins of different complexity, amino acids, amides, various bases of the purine, pyridine and pyrimidine series and other nitrogen-containing organic compounds.
4. Lignins and their derivatives. This group includes not only the formed lignins of higher plants and “precursors of lignin”, but also initial products of their decomposition.
5. Tannic substances in simple and condensed forms.
6. Resins and terpenes.

In soil there are present, in addition, various organic acids, aromatic materials, hydrocarbons, alcohols and other groups of compounds.

A whole range of chemically individual compounds was isolated from the soil and identified by many investigators. As already mentioned in the preceding chapter, systematic studies in this direction were carried out by the American investigators, Schreiner and Shorey, and co-workers (1908–1938).

The list of organic substances of non-specific nature isolated from soils by numerous investigators was classified by Shmuk (1930) and Maiwald (1931) as follows:

1. *Carbohydrates*:
(a) Pentoses, pentosans; (b) hexoses; (c) cellulose and early products of its decomposition.

2. *Hydrocarbons:*

Paraffin

3. *Organic acids of the fatty series and their esters:*Oxalic acid $(\text{COOH})_2$ Succinic acid $(\text{CH}_2\text{COOH})_2$ Saccharic acid $(\text{CHOH})_4(\text{COOH})_2$ Crotonic acid $\text{CH}_3\text{CH}=\text{CHCOOH}$ Lignoceric acid $\text{C}_{24}\text{H}_{48}\text{O}_2$ Monohydroxystearic acid $\text{C}_{18}\text{H}_{36}\text{O}_3$ Dihydroxystearic acid $\text{C}_{18}\text{H}_{36}\text{O}_4$ Acrylic acid $\text{CH}_2=\text{CHCOOH}$ Benzoic acid $\text{C}_6\text{H}_5\text{COOH}$

and a number of others

4. *Alcohols:*Mannitol $\text{C}_6\text{H}_8(\text{OH})_6$ 5. *Esters:*

Glycerides of caproic and oleic acids

6. *Aldehydes:*Salicylaldehyde (*o*-hydroxybenzaldehyde) $\text{C}_6\text{H}_4\text{OHCHO}$ Vanillin $\text{C}_6\text{H}_3(\text{OCH}_3)\text{OHCHO}$

and a number of others

7. *Resins:*

Resin acids and their derivatives

8. *Nitrogen-containing compounds:*Trimethylamine $(\text{CH}_3)_3\text{N}$ Choline $\text{C}_5\text{H}_{15}\text{O}_2\text{N}$ Histidine $\text{C}_6\text{H}_9\text{O}_2\text{N}_3$ Arginine $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_4$ Lysine $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_2$ Hypoxanthine, cytosine $\text{C}_4\text{H}_5\text{ON}_3$ Xanthine $\text{C}_5\text{H}_4\text{O}_2\text{N}_4$ Creatinine $\text{C}_4\text{H}_2\text{ON}_3$

Derivatives of pyridine

A number of monoamino-acids

During 1930–40, interest in the non-specific organic compounds of soil humus began to decline due, no doubt, to the increasing attention paid to strictly humus substances.

Shorey (1938) isolated and identified allantoin. Shorey and Martin (1930), Waksman and Reuszer (1932), Tyurin and Kononova (1934), Norman and Bartholomew (1943) detected polyuronides in soils; these are partly constituents of plant tissues (hemicelluloses) but mainly products of resynthesis—bacterial slime, as is well known, contains polyuronic complexes. Rudakov and Birkel' (1949) showed that uronic acids are exuded from root systems of the living plant with the participation of bacteria producing protopectinase.

The detection by Enders of methylglyoxal ($\text{CH}_3\text{COCO}\text{H}$) in soils is of interest. As is well known, methylglyoxal (according to Neuberg) is an intermediate product in carbohydrate fermentation. Moreover, Hibbert (1942) regarded methylglyoxal as a possible primary structural element of protolignins. Being thus genetically related to the two main constituents of plant tissues—carbohydrates and lignins—methylglyoxal serves as a "bridge" between the lignin and cellulose theories on the origin of humic acids.

Of interest are the data presented by Forsyth (1947), who detected glycosides among the various products present in acid solution after humic acids were precipitated from alkali extract; these are ester-like compounds of hexoses (most often d-glucoses) with various other compounds belonging mainly to the aromatic series; since they contain the $-\text{O}-$ group, glycosides possess a high capacity for reactions of condensation and self-condensation and may, therefore, serve as the primary source for the formation of complex substances of synthetic nature such as humus substances.

An essential difficulty in studying organic compounds of an individual nature is the fact that they only occur in small amounts in the soil. Thus in a study of their nature and identification by conventional chemical procedures, which require relatively large quantities of substances, large soil samples are necessary.

New methods of investigation (in particular chromatography and optical methods) that enable substances to be detected and identified in small amounts have stimulated the current renewed interest in the study of soil organic substances of an individual nature. At the same time new facts showing the diverse function of these substances have also contributed to an increased interest by research workers.

In the aqueous, alcoholic and salt extracts from soils, a number of amino acids have been detected and quantitatively determined by chromatography (Davidson *et al.*, 1951; Dadd, Fowden and Pearsall, 1953; Simonart and Peeters, 1954; Payne, Rouatt and Katznelson, 1956; Paul

and Schmidt, 1960, 1961; Ivashchkevich, Kuprevich and Shcherbakova, 1963). Among the amino acids found were aspartic and glutamic acids, alanine, glycine, serine, leucine and iso-leucine, valine-methionine, lysine, ornithine, phenylalanine and tyrosine.

Nagar (1953, 1962) has shown that free monosaccharides are present in soils.

Some low-molecular-weight organic acids (acetic, fumaric, lactic and some others) have been isolated from soils by Schwartz, Varner and Martin (1954) and Takijima (1961), and from soil extracts and soil solution by Kaurichev *et al.* (1963) and Skrynnikova (1959).

Polysaccharides and their derivatives are an interesting and, as we shall see later, important group of substances that have recently attracted the attention of research workers. The presence of this group of substances (in particular polyuronic acids) in the soil is explained by the fact that they are components of plant tissue and of the slime from various organisms, particularly micro-organisms (Forsyth, 1947, 1949, 1950; Fuller, 1947; Duff, 1952, 1954, 1961; Hearns, Lynch and Cotnoir, 1958; Graveland and Lynch, 1961; Whistler and Kirby, 1956; Müller, Mehta and Deuel 1960; Parsons and Tinsley, 1961; Gupta, 1962; Krym, 1962; Mortensen and Schwendinger, 1963).

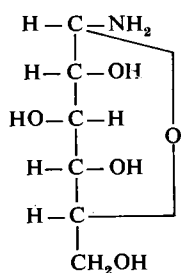
Using a new method in which polyuronic acids are estimated by means of carbazole, a number of authors (Lynch, Hearns and Cotnoir, 1957; Dubach and Lynch, 1959; Deuel *et al.*, 1958a, b, 1960) have determined these acids more precisely in the soil; the polyuronic acid content was lower than that indicated from previous work (Shorey and Martin, 1930; Waksman and Reuszer, 1932; Tyurin and Kononova, 1934; Norman and Bartholomew, 1943) in which it had been determined by the evolution of CO₂ when the soil was boiled with 12% HCl.

Among the derivatives of uronic acids, an important place is occupied by amino sugars, which represent mainly the products of microbial resynthesis (Bremner, 1951, 1958; Bremner and Shaw, 1954; Stevenson, 1956, 1957; Sowden 1955).

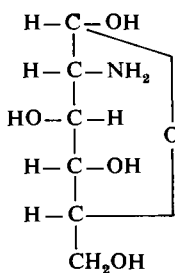
Substances of the amino sugar-type (glucosamines) are also formed during the decomposition of chitin, which is a component of some fungi, algae and the shells of some invertebrates. When the temperature is raised or when catalysts are present in the medium, glucosamine is capable of condensing and this has led to the assumption that this group of compounds takes part in the formation of humus substances of the melanoidin type.

Glucosides, which were detected by Forsyth (1947) in the solutions

left after humic acids had been precipitated from alkaline extracts, possess a high chemical reactivity and a tendency to condensation reactions.



N-glucoside



d-glucosamine

Recently it has become clear that polyphenols, which have been shown to be present in soils, in leaf fall and in forest litter, are important in the processes of weathering and podzol formation (Bloomfield, 1957; Davies, Coulson and Lewis, 1960; Coffin and Delong, 1960).

The great diversity of soil organic compounds of an individual nature has been demonstrated by Jacquin (1959, 1960); using partition paper chromatography, he detected amino acids, polyphenols, polysaccharides and organic acids in extracts obtained from podzolic and mull soils at room temperature with 0.5N HCl. Kaurichev and Nozdrunova (1961) found tannins, amino acids and low-molecular-weight organic acids in soils and in aqueous extracts from leaf fall.

Similar results have been obtained by Aleksandrova (1960); using partition paper chromatography, she established that amino acids, low-molecular-weight organic acids and polyphenol-like substances (Fig. 1, A, B and C) were present in natural solutions squeezed from peat and podzolic soils in a press (see Chapter 8, section "Methods of studying the composition of organic matter in soil solutions").

All the work cited, which reveals that various organic compounds of an individual nature are present in soils, provides a basis for assuming that these substances widely participate in pedological processes (weathering, decomposition of minerals, geochemistry of a number of elements, structure formation) and also in plant nutrition, and supply the plant with biologically active substances (see Chapter 4).

It is clear that greater attention should be paid to the study of the composition and properties of soil organic compounds of an individual nature. It cannot be assumed that, because these compounds occur in small

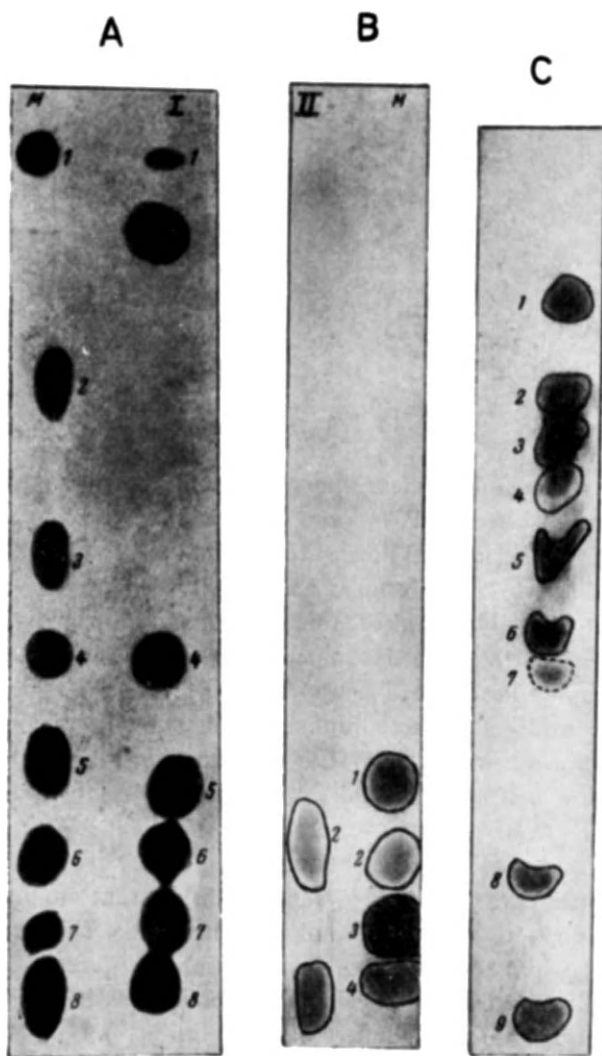


FIG. 1. Chromatograms of organic substances in soil solutions.

- A. Organic acids; M. standard solutions; I. solution from upland moor peat.
 1. oxalic acid; 2. tartaric acid; 3. citric acid; 4. malic acid; 5. lactic acid;
 6. succinic acid; 7. glutamic acid; 8. adipic acid.
- B. Compounds of aromatic nature; M. standard solutions; II. solution from hypnum peat.
 1. pyrogallol; 2. protocatechuic acid; 3. pyrocatechol; 4. salicylic acid.
- C. Amino acid composition of the hydrolysate of solution from high peat. 1. lysine;
 2. aspartic acid; 3. glycine; 4. glutamic acid; 5. threonine; 6. alanine; 7. proline;
 8. valine; 9. phenylalanine.

amounts in the soil, they are of lesser interest, as many of their functions (action as stimulants and inhibitors of plant growth, as antibiotics and as vitamins) are manifested only when they are applied in small amounts.

STRICTLY HUMUS SUBSTANCES IN SOIL ORGANIC MATTER

Although there is no cause at present to doubt the actual existence in the soil of humus substances as natural compounds, their composition is not yet completely clear. The main reason for this is the insufficient characterization of the nature and structure of the different representatives of humus substances and also of their origin.

These data are necessary for solving the problem of the genetic relationship and essential differences between these substances, which is a basis for their rational classification.

Methods of isolating humus substances from the soil

Only a small part of the humus substances in the soil are in a free state; a larger part occurs with various forms of linkage to the mineral part of the soil. This linkage must be destroyed if humus substances are to be converted into a soluble state.

A number of investigators have criticized the common practice of isolating humus substances from the soil by alkaline solution and attempts have been made to replace this solution by milder solvents. As long ago as the 1930's, investigators began to use the neutral solutions of the salts of mineral acids (e.g. NaF) and also the salts of oxalic and other low-molecular-weight organic acids for this purpose (Simon, 1929, 1930; Pozdena, 1937a, 1937b; etc.).

More recently, various inorganic and organic solvents have been used for isolating humus substances from soil (Bremner *et al.*, 1946, 1949; Hamy and Leroy, 1952; Maes and Leenheer, 1954; Dragunova, 1954; Okuda and Hori, 1956; Martin and Reeve, 1955, 1957; Kosaka and Izeki, 1956; Tinsley, 1956; Parsons and Tinsley, 1960; Tinsley and Salam, 1961; Choudhri and Stevenson, 1957; Schnitzer, Wright and Desjardins, 1958; Evans, 1959; Kawaguchi and Kyuma, 1959; Aleksandrova, 1960a; Dubach, Metha and Deuel, 1961).

Much attention has been paid to neutral salts of mineral acids, in particular sodium pyrophosphate. The action of pyrophosphate and also some neutral salts of organic acids (e.g. sodium salts of oxalic, tartaric, citric

and other acids) in isolating humus substances from the soil depends upon their ability to form insoluble precipitates or soluble complexes with calcium, iron, aluminium and other polyvalent cations to which humus substances in the soil are linked. As a result of these reactions, humus substances are converted into a soluble state.

However, a number of authors in comparable investigations have shown that these solutions extract smaller quantities of organic substances from the majority of soils in which humus substances occur in complex forms of linkage with the mineral part of the soil, than the solutions of alkalis. Using neutral solutions of sodium pyrophosphate and sodium fluoride, Schnitzer, Wright and Desjardins could isolate a large proportion of the organic carbon only from the B-horizon of a podzolic soil; this proportion was similar to that found when 0.1 N NaOH was used (Table 3). From horizon A_0 of the same soil, $\text{Na}_4\text{P}_2\text{O}_7$ and NaF extracted much smaller quantities of organic substances than 0.1 N NaOH.

TABLE 3. ORGANIC CARBON EXTRACTED FROM PODZOLIC SOIL BY VARIOUS SOLUTIONS (as % of total soil carbon)
(Schnitzer, Wright and Desjardins, 1958)

Horizon	Solutions						
	$\text{Na}_4\text{P}_2\text{O}_7$ pH 9.8	$\text{Na}_4\text{P}_2\text{O}_7$ pH 7.0	NaF pH 8.2	NaF pH 7.3	Na_2CO_3	NaOH	Na_2 EDTA
A_0	6.1	5.5	6.6	4.4	8.3	24.8	Trace
B	91.7	82.6	88.4	88.7	92.3	96.3	86.0

We obtained analogous results while trying out various methods for extracting humus substances from the soil (Kononova and Bel'chikova, 1961). From podzolic, chernozem, chestnut, and serozem soils the largest amounts of humus substances were extracted by repeated treatment of the decalcified soil with 0.1 N NaOH (Tyurin's method). Similar amounts of humus substances are extracted by a single treatment of the soil with a mixture of 0.1 N $\text{Na}_4\text{P}_2\text{O}_7$ and 0.1 N NaOH (pH ~13), and so we recommended the use of this mixture in a rapid method for determining the composition of humus (see Chapter 8, section "Rapid method of determining the composition of humus in mineral soils").

Significantly smaller quantities of humus substances are extracted from the soil with 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ solution (Table 4). Even from the humus-illuvial horizon of strongly podzolic soils 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ solution extracts

about 60 per cent of the total organic matter (Kononova and Titova, 1961; Titova, 1962).

TABLE 4. HUMUS SUBSTANCE CARBON EXTRACTED FROM THE SOIL BY VARIOUS SOLUTIONS (as % of total soil carbon)

Soil (arable layer)	Strongly podzolic soil, % org. C = 1.20		Chernozem % org. C = 5.00		Chestnut soil % org. C = 1.78		Serozem % org. C = 0.82	
Solution	Humic acids	Fulvic acids	Humic acids	Fulvic acids	Humic acids	Fulvic acids	Humic acids	Fulvic acids
0.1 M $\text{Na}_4\text{P}_2\text{O}_7$								
pH 7.4	5.9	15.8	11.8	6.2	6.7	7.9	4.9	12.2
pH 8.3	10.0	14.2	22.4	6.2	10.7	8.4	8.5	11.0
0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ + 0.1 N NaOH (pH 13)	22.5	30.0	37.0	13.0	19.7	14.6	17.1	20.7
0.1 N NaOH (Tyurin's method)	18.3	21.7	37.4	14.2	19.1	12.9	14.6	14.6

The solution of 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ extracts humus substances completely from peat soils, where these substances occur in a free state or in the form of calcium, iron or aluminium humates (Drozdova, 1959a).

For more complete extraction of humus substances from the soil, the most practicable method is still treatment with alkali solutions; it has been shown that this method does not change the nature of humus substances essentially.

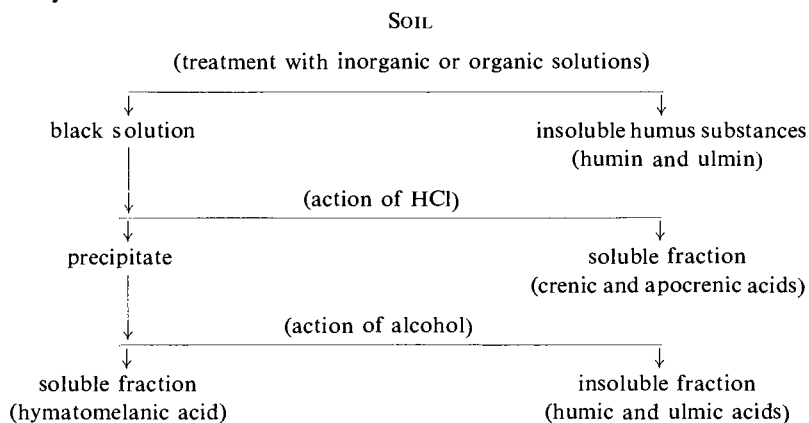
Thus, Scheffer and Welte (1950 a, b) and Welte (1952) found no essential differences between the character of the light-absorption curves of solutions of humic acids isolated by means of 0.5% NaOH and those isolated with 1% NaF. Further, Rȳdalevskaya and Skorokhod (1951) noticed that there were no essential differences in the elementary composition and content of carboxyl groups (COOH) between humic acids from different soils and peats, whether isolated with 1% NaF or with 0.1 N NaOH. Similar conclusions can be drawn from the works of Aleksandrova (1953) and Fat'yanov (1953).

For a more complete extraction (particularly from soils with a high content of exchangeable calcium and CaCO_3) a preliminary treatment of

the soil with dilute acid (2% HCl) is to be recommended. At the same time a partial hydrolysis of organic compounds of individual nature (e.g. hemicelluloses), whose preliminary removal from the soil is desirable to prevent subsequent contamination of the strictly humus substances, takes place.

A difficulty experienced during studies of the nature and properties of humus substances is their high ash content, although it is possible to decrease the ash content of the extracted preparations of humic acid substantially by repeated reprecipitation, electrodialysis and filtration through ion-exchange resins.

According to ideas that originated in the previous century, the classification of humus substances into groups is based on colour and behaviour towards solvents (see the following scheme). In the light of contemporary data these principles of classification can no longer be regarded as satisfactory.



Within this scheme, the main groups of humus substances are: (1) humic and ulmic acids, (2) crenic and apocrenic acids, (3) hymatomelanic acid, (4) humin and ulmin. We shall examine each group of substances according to this scheme, using new data characterizing their nature, structure and properties.

Humic acids of soil humus

Included under the term humic acid is the group of substances normally extracted from the soil by solutions (NaOH, KOH, NH_4OH , NaHCO_3 , $\text{Na}_4\text{P}_2\text{O}_7$, NaF, sodium oxalate, urea, etc.) and forming amorphous precipitates with acids; this is one of the characteristic groups of soil humus substances, as investigators pointed out even as early as the last century.

Naturally, over a long period, ideas on the nature of humic acids have changed considerably and no longer can they be regarded as completely identical with the views of Sprengel, Berzelius, German and Mulder, who are accredited with the first of the more reliable investigations on this group of substances.

Thus, in contrast to previous theories on humic acids according to which they were regarded as chemically individual compounds (some investigators at a later date, e.g. Odén (1919), Strache and Lant (1924), developed similar theories), the conception of "humic acids" at the present time is of a group of substances having a common form of structure although not completely identical with one another.

Similarly, present-day ideas on the origin and mechanism of formation of humic acids differ from those previously held. In the last century, humic acids were regarded as products of the oxidation and dehydration of single substances, mainly carbohydrates. However, further investigations have shown that several substances participate in the formation of humic acids.

This does not mean that humic acids are an indeterminate mixture of substances as many investigators of the last century and beginning of the present were inclined to believe. With the accumulation of data on the humic acids of different soils, certain common features of their structure have emerged. Moreover, variations in their elementary composition are limited to a fairly narrow range. We may thus conclude, firstly, that substances belonging to the same class of organic compounds participate in the formation of humic acids and, secondly, that these substances are present in the humic-acid molecules in definite ratios.

These theories, which appear at first sight to be unrelated, become clearer when contemporary ideas, in which humic acids are regarded as high-molecular-weight compounds formed during the condensation of two, or perhaps three, different substances, are taken into consideration.

We shall consider data forming the basis of contemporary theories on humic acids.

The elementary composition of humic acids. At the present time, comprehensive information is available on the elementary composition of the humic acids isolated from different soils. Some investigators draw attention to a similarity in the values of this criterion in humic acids of different origin. Gillam (1940), for instance, found no essential differences between the elementary composition of humic acids isolated from forest soil, meadow soil and manured soil.

Tishchenko and Rýdalevskaya (1936), however, were able to show regular changes in the elementary composition of humic acids, reflecting

the natural conditions under which the humus was formed, in a series of soils ranging from podzolic soils to chernozems and further, to chestnut soils; in the humic acids of this soil series it was found that the percentage of carbon increased and that of hydrogen and oxygen decreased, the decrease of hydrogen being greater than that of oxygen so that the O:H ratio became wider. This indicates the occurrence of a larger number of hydroxyl groups and lower oxidation in humic acids from podzolic soils than in humic acids from chernozem where the processes of dehydration and oxidation proceed much further. Hence, on passing from podzolic soils to chernozems, the nature of humic acids becomes more complex (Tables 5 and 20).

TABLE 5. ELEMENTARY COMPOSITION OF HUMIC ACIDS FROM DIFFERENT SOILS

Soils from which humic acids were isolated	%C	%H	%N	%O	C:N	C:H	O:H	Author
Podzolic soil	52.39	4.82	3.74	39.05	14.0	10.9	8.1	Tishchenko and Rȳdalevskaya (1936)
Rendzina	54.90	4.36	4.07	36.67	13.5	12.6	8.4	
Degraded chernozem	56.34	3.54	3.58	36.65	15.7	15.9	10.3	
Deep chernozem	57.47	3.38	3.78	35.37	15.2	17.0	10.4	
Ordinary chernozem	58.37	3.26	3.70	34.67	15.7	17.9	10.6	
Chestnut soil	58.56	3.40	4.09	33.95	14.3	17.2	10.0	
Podzolic soil	56.67	4.79	5.14	33.40	11.0	11.8	7.0	Natkina (1940)
Ordinary chernozem	62.55	2.78	3.32	31.35	18.8	22.5	11.3	
Columnar solonets	59.21	3.83	4.28	32.68	13.8	15.4	8.5	Kononova (1943)

The data presented by Tishchenko and Rȳdalevskaya were confirmed by other investigators (Natkina, 1940; Gemmerling 1946; Remezov, 1945; Dragunov, 1948; Kononova, 1956).

Functional groups of humic acids. Most of the available data on the determination of functional groups are related to humic acids isolated from peat and coal. Although earlier works dealing with the presence of functional groups in humic acids (Sestini, 1902) will not be discussed in detail, it is worth mentioning that Odén, on the basis of his investigations, concluded that a molecule of humic acid from peat contains four carboxyl groups and he reflected this in the approximate formula $C_{60}H_{52}O_{24}(COOH)_4$ with a molecular weight of 1350.

Fuchs and Stengel (1929) determined the following functional groups in humic acid from brown coal: carboxyl groups (by means of methylation with methanolic HCl) and phenolic hydroxyl groups (by means of further

exhaustive methylation using diazomethane on the ester obtained from the former treatment). Fuchs, on the basis of his experimental results, thought it probable that four carboxyl and three phenolic groups were present in humic acid from brown coal; in humic acid there may also be present alcoholic (OH) groups which are not acidic and are not methylated with diazomethane, but, like phenolic hydroxyl groups, are methylated with dimethyl sulphate. Stadnikov and Korzhev reached similar conclusions with regard to the humic acids from peat, detecting in them four carboxyl and three phenolic groups. Although data on the humic acids from peat and coal will not be discussed further, it should be mentioned that Shmuk demonstrated the presence of carboxyl groups in soil humic acids by the formation of ethyl esters during esterification with ethanolic HCl. For the same humic acids (from chernozem), Shmuk demonstrated the presence of phenolic and hydroxylic groups by means of the formation of complex esters of benzoic acid during their reaction with benzoyl chloride. Shmuk's investigations, however, were of a qualitative nature.

Later, the works of Tishchenko and Rydalevskaya (1936), Natkina (1940), Gemmerling (1946) and Dragunov (1948) showed the presence of three to four carboxyl groups in humic acids; for phenolic hydroxyl groups, the data presented by these authors are somewhat contradictory. Thus, Tishchenko and Rydalevskaya (1936, Table 6) found that humic acids from various soils, like those from peat and recently formed coal, contain three phenolic groups. However, Natkina gave higher numbers of phenolic groups—for podzolic soil, six to seven, and for chernozem, four. Dragunov (1948) detected four phenolic groups in humic acids from podzolic soil and five in humic acid from chernozem. It is possible that these discrepancies are explained by actual differences in the nature of the humic acids investigated; however, the possibility of cross-methylation of the functional groups by the methods employed should also be taken into account (see Scheffer and Ulrich, 1960, pp. 47–48).

Besides carboxyl, phenolic and alcoholic groups, humic acids also contain methoxyl groups OCH_3 up to 1–2 per cent in amount (Table 6).

Apparently, a quinoid group is present in humic acids. It may also be assumed that in soil humic acids, double-bond carbon groupings $-\text{CH}=\text{CH}-$ occur; this is indicated by their ease of chlorination (Mulder; Shmuk, 1924; and others). Finally, the carbonyl group may occur in soil humic acids.

Many investigators, e.g. Ubaldini (1937), Dragunov and co-workers (1948) and Kukharenko (1950), have shown by chemical methods that

TABLE 6. THE NUMBER OF FUNCTIONAL GROUPS IN SOIL HUMIC ACIDS

Soils from which humic acids were isolated	Initial methoxyl	Methoxyl of COOH groups		Methoxyl of phenolic groups (OH)		Author
		%	Number of groups	%	Number of groups	
Podzolic soil	0.79	9.26	4	7.48	3	Tishchenko and Rydalevskaya (1936)
Peat soil	1.57	9.50	4	7.00	3	
Rendzina	1.18	9.44	4	7.07	3	
Degraded chernozem	0.34	8.97	4	7.17	3	
Deep chernozem	0.69	9.05	4	7.12	3	
Ordinary chernozem	0.52	9.68	4	7.49	3	
Chestnut-like chernozem	0.51	9.42	4	7.44	3	Natkina (1940)
Ordinary chernozem	0.73	9.12	4	8.98	4	
Podzolic soil	2.49	9.37	4	14.40	6-7	

carbonyl groups are present, and in recent years Kasatochkin and Zil'berbrand (1956), Ziechmann and Pawelke (1959), Orlov and co-authors (1962) amongst others, have used infra-red spectroscopy to establish that humic acids contain these groups.

The presence of functional carboxyl and phenolic hydroxyl (OH) groups explains one extremely important property of humic acids—their participation in exchange reactions. The exchange-absorption capacity of various humic acids is shown by the following values:

Soils from which the humic acids were isolated	Exchange-absorption capacity (m eq/100 g substance)	Author
Chernozem	474.5	Natkina (1940)
Podzolic soil	345.2	
Dark chestnut soil	483.3	Kononova (1943)
Columnar solonets	430.0	

The data given characterize only the replacement of the hydrogen of carboxyl groups, since the determinations were carried out in neutral conditions (with Ca acetate at pH 7.0). In alkaline conditions, the hydrogen

of phenolic hydroxyl groups also takes part in the reaction. This was demonstrated for peat humic acids by Stadnikov (1932) and co-workers. Khainskiĭ (1936), using the potentiometric titration method, showed that, in neutral conditions, the hydrogen of carboxyl groups of peat humic acids is replaced, and that successive alkalinization of the medium causes a sharp drop in the potentiometric curve, evidently coinciding with the replacement of the hydrogen of phenolic hydroxyl groups.

Of interest are the results for soil humic acids obtained by Rȳdalevskaya and Tishchenko (1944), who demonstrated a succession in the replacement of the hydrogen of functional groups at different pH values (Table 7).

TABLE 7. THE ABSORPTION CAPACITY OF HUMIC ACID AT DIFFERENT pH IN MILLI-EQUIVALENTS PER 100 g (Rȳdalevskaya and Tishchenko, 1944)

Soil from which humic acids were isolated	pH 4·5		pH 6·4		pH 8·1	
	m eq	Number of groups	m eq	Number of groups	m eq	Number of groups
Chernozem	292·2	4	432·9	6	590·5	8
Podzolic soil	243·0	3·4	410·0	5·6	548·7	7·8
Bog-peat soil	170·0	2·3	286·3	4	400·0	5

These data indicate that the participation of humic acids in exchange reactions depends on the conditions of the soil medium: the higher the soil reaction, the greater the number of functional groups of humic acids participating on the exchange reactions.

Dialysed solutions of humic acids have a pH of approximately 3·5; they are weakly dissociated organic acids with an equivalence point at a pH of about 8·0–9·0 as can be seen from the potentiometric titration curves in Fig. 2 (Puri, 1949; Puustjärvi, 1955; Roy, 1957; Pommer and Breger, 1960; and others).

The fact that humic acids are weakly dissociated determines, to a large degree, an important property of the soil—its buffering capacity.

It has now been established that humic acids have a complex structure; at least two main components (or so-called “structural units”)—compounds of phenolic or quinoid nature and nitrogen-containing compounds (amino-acids and peptides)—participate in the formation of their molecule.

There are reasons for supposing that humic-acid molecules also contain a third component — substances of carbohydrate nature.

The aromatic ring of humic acids. Hoppe-Seyler was the first to demonstrate the presence of the aromatic ring in humic acids obtained from peat and brown coal by fusion of the latter with concentrated KOH at a temperature of 245° C; among the fusion products he detected pyrocatechol and protocatechuic (3,4-dihydroxybenzoic) acid.

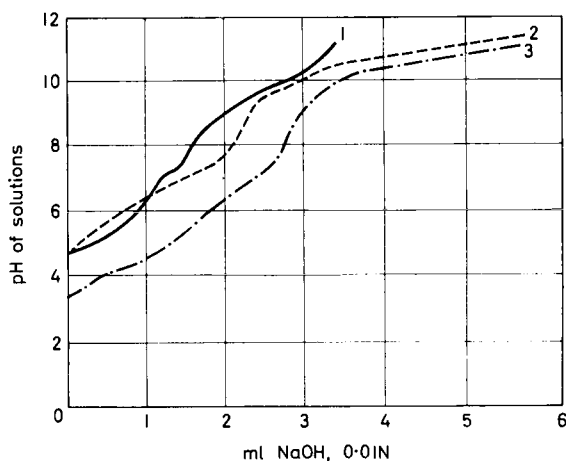


FIG. 2. Potentiometric titration curves of humus substances (Bel'chikova).

1. Humic acids of sod-podzolic soil; 2. Humic acids of ordinary chernozem; 3. Fulvic acids of ordinary chernozem.

The study of the skeleton of humic acids from peat and coal received particular attention during the 1920's, the formulation period of the lignin theory on the origin of humic acids. Tropsch and Schollenberg (1921) studied the fusion products of humic acid of brown coal and separated isophthalic, 5-hydroxyisophthalic and *m*-hydroxybenzoic acids from these products. The aromatic nature of the basic skeleton of humic acids was shown by the investigations of Hofman and Greve, who found that during the destructive distillation of these acids phenols were formed in considerable amounts¹.

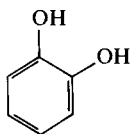
Investigations carried out under mild conditions are of great interest in establishing the aromatic nature of humic acids. Such were the works of Fuchs and Stengel (1929–1930), who carried out the oxidation of humic

¹ From Stadnikov (1932), *The Chemistry of Peat*, Moscow: Gostekhizdat.

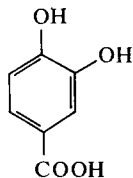
acids from brown coal with dilute nitric acid (1:1) at 90° C for 1½ hours. Among the oxidation products, they were able to detect nitrophenols and a mixture of benzene-carboxylic acids. The total yield of crystalline products was 10 per cent of the original amount of humic acid. Zetsche and Reinhart (1939), by reduction with amalgam and zinc dust, demonstrated the aromatic nature of humic acid; among the products of the reduction were substances of phenolic nature.

Investigations of the aromatic ring of humic acids from peat and coal, carried out during the 1920's, were closely linked with studies on lignin, whose aromatic nature was established by many investigators (Klason, 1922–1932; Freudenberg and Harder, 1927–1928; and others). Parallel studies on humic-acid derivatives and lignin, carried out by Fuchs, Fischer and other investigators, showed their close similarity, and this was one of the arguments in favour of a lignin origin of humic acids from peat and coal.

With regard to soil humic acids, Shmuk (1924) was the first to show the presence of the aromatic ring in humic acid from chernozem, which he subjected to alkali fusion by Hoppe-Seyler's method. Among the fusion products he found firstly, indole, skatole and derivatives of pyrrole, indicating the presence of aromatic amino acids in the humic-acid molecule, and secondly, derivatives of polyphenols and protocatechuic acid. Since protein does not yield these products in significant amounts, Shmuk attributed their presence in humic acid to lignin and tannic substances.



pyrocatechol



protocatechuic acid

Dragunov (1948) subjected humic acids from podzolic and chernzecei soils to alkali fusion with concentrated KOH at a temperature of 270–280° for 1½ hours (Table 8). In this way, he was able to demonstrate the presence of aromatic compounds of polyphenol type in humic acids from both soil and peat. Among the fusion products of humic acids from podzolic soils and from peat he found protocatechuic acid, and in the fusion products of humic acid from chernozem, a trihydroxyphenol (according to Dragunov's assumption, pyrogallol) was detected.

TABLE 8. SUBSTANCES ISOLATED AFTER THE FUSION OF HUMIC ACIDS WITH KOH AS A PERCENTAGE OF THE SAMPLE (Dragunov, 1948)

Material from which humic acid was isolated	Yield of aromatic substances	Pyro-catechol	Proto-catechuic acid	Substances soluble in benzene	Substances insoluble in benzene
Peat	—	0	15.0	—	—
Chernozem soil	7.5	0	0	1.5	4.0
Medium podzolic soil	7.3	traces	5.0	—	—

Kukharensko and Savel'ev (1951) hydrogenated the humic acid from various stages in coal formation, using a dioxan medium in the presence of a nickel catalyst and found carboxylic acids, phenols and their derivatives. A theoretical scheme for the decomposition products of humic acids, compiled by Flaig (1958a), is given in Fig. 3.

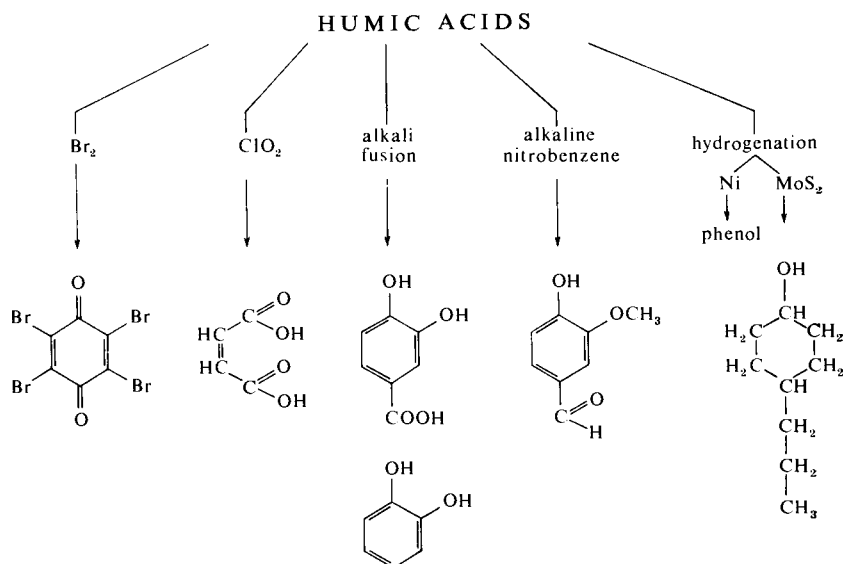


FIG. 3. Products of the decomposition of humic acid (Flaig, 1958).

Recently, Scharpenseel (1960), using partition paper chromatography, detected among the products of alkaline fusion and nitrobenzene oxidation of soil humic acids aromatic compounds of the pyrocatechol, pyrogallol and protocatechuic acid type.

Aqueous, acid and alkaline hydrolysis of humic acids from soils and peats has yielded various products of an aromatic nature such as vanillin,

syringaldehyde, vanillic acid, derivatives of catechins and benzoic acid (Greene and Steelink, 1962; Jakab *et al.*, 1961; Jacquin, 1962; Scheffer and Kickuth, 1962; Hayashi and Nagai, 1961; Murphy and Moore, 1960). The presence of lignin components (vanillin and syringaldehyde) in the hydrolyzates indicates that lignin and other plant substances participate in humic acid formation.

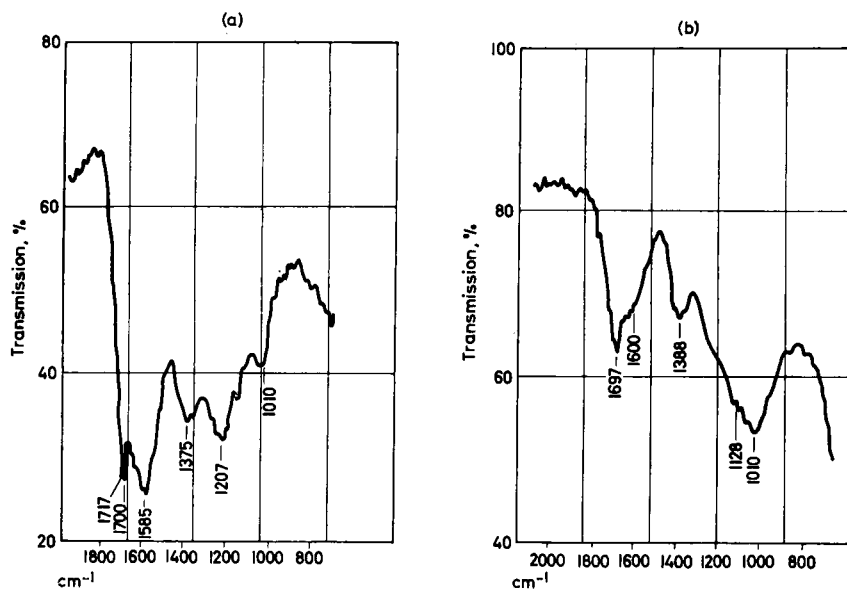


FIG. 4. Infra-red spectra of (a) humic acid from a chernozem; and (b) of fulvic acid from a sod-podzolic soil.

Porphyrin-type substances have been found in humic acids isolated from the A- and B-horizons of podzols suggesting that chlorophyll from plant residues may take part in the formation of humic acids (Kumada and Sato, 1962).

Results from infra-red spectroscopy have shown the aromatic nature of soil and peat humic acids (Kasatochkin and Zil'berbrand, 1956; Kumada and Aizawa, 1958; Ziechmann and Pawelke, 1959; Ziechmann and Scholz, 1960; Goulden and Jenkinson, 1959).

Figure 4a shows the infra-red spectrum of humic acid from a chernozem recorded in the laboratory of Prof. Kasatochkin (Institute of Mineral Fuels, Academy of Sciences USSR).

The infra-red spectrum (Fig. 4) of humic acids from a chernozem shows absorption bands characteristic of vibrations in the following

groups of atoms: vibration of carboxyl C=O (carbonyl) in aliphatic and aromatic acids at 1700 cm^{-1} ($5.88\text{ }\mu$); stretching vibration of conjugated carbon double bonds C=C at 1585 cm^{-1} ($6.31\text{ }\mu$), showing that an aromatic carbon net is present. The high intensity of this absorption band may be explained by enhancement at the expense of quinones and hydroxyquinones and also of nitrogen C=N (cyclic forms of nitrogen are characteristic of humic acids from chernozems). The band at 1375 cm^{-1} ($7.28\text{ }\mu$) characterizes the CH_3 and CH_2 of aliphatic groups. The bands in the region 1207 cm^{-1} ($8.29\text{ }\mu$) and 1010 cm^{-1} ($9.9\text{ }\mu$) correspond with the stretching vibration of C—O or bending vibration of OH (alcohols, esters, acids).

In the course of comparative studies on humic acids from different soils, authors note the same typical character of the infra-red spectra, which may serve as an indication that the structure of these acids is similar (Scharpenseel and Albersmeyer, 1960; U Dzhi-khua, 1959; Orlov *et al.*, 1962).

Together with humic acids of aromatic nature, also occur humic acids with masked aromatic rings or without aromatic rings; the melanoidins are related to them.

Reducing substances in the composition of soil humic acids. It is not yet clear whether or not the humic-acid molecule contains reducing substances, although this information would be of considerable interest from the point of view of the nature and origin of humic acid. Reinitzer (1900) found that humus substances have the capacity for reducing Fehling's solution, indicating that they contain the aldehyde group. However, Shmuk (1924) did not detect reducing substances during an investigation of humic acid from chernozem, and he assumed, therefore, that Reinitzer investigated insufficiently pure humic acid, the reducing capacity of which was attributable to the admixture of carbohydrates.

Subsequent works (Dragunov, 1948, 1950) confirmed the presence of reducing substances in soil humic acids, their amount depending, however, on the method of purification of the solution obtained by hydrolysis of the humic acids (Table 9).

Thus, if the acid hydrolysate is not subjected to the purification commonly employed with plant material—by means of lead acetate and Ba(OH)_2 —then the content of reducing substances in humic acid from chernozem reaches a fairly considerable value—11.09 per cent. However, if the hydrolysate is subjected to purification the amount of reducing substances is only 3.33 per cent. Hence, the method of purification used removes a large part of the reducing substances from the solution.

TABLE 9. THE CONTENT OF REDUCING SUBSTANCES IN HUMIC ACIDS

Humic acids	Reducing substances (%)	Method of hydrolysis	Author
From podzolic soil (Moscow region)	14.73	5% HCl without subsequent purification	} Dragunov (1948)
From chernozem (Kursk region)	11.09	„ „	
„ „	3.33	5% HCl with subsequent purification of the hydrolysate	Bel'chikova

Some investigators (Stevenson, Marks, Varner and Martin, 1952; Lynch, Wright and Olney, 1957; Wright, Schnitzer and Levick, 1958; Coulson, Davies and Khan, 1959a; Hayashi and Nagai, 1961; Johnston, 1961), using partition paper-chromatography, demonstrated carbohydrates—pentoses, hexoses, galacturonic acid and other compounds of carbohydrate nature—in the acid hydrolysate of humic acids.

At present, we cannot say for certain whether reducing substances are a contaminant or part of the molecule of humic acid. Some data support the latter hypothesis; considering that products of the resynthesis of microbial plasma undoubtedly participate in the formation of the humic-acid molecule, and as carbohydrates of specific nature, including polyuronides, are a common component of bacterial slime, then the presence of carbohydrate residues in the humic-acid molecule would not be surprising.

The nitrogen-containing part of humic acids. At the present time there is no doubt that soil humic acids contain nitrogen, the amount being approximately 3.5–5 per cent. The investigators of the last century thought that humic acids were of carbohydrate origin and regarded the nitrogen in them as an accidental admixture. This view that humic acids were nitrogen-free compounds was later shared by investigators of the chemistry of humus substances of peat and coal (Odén, Fischer, Schrader, Stadnikov, Fuchs and others) for it accorded with their theory on the lignin origin of humic acids.

However, for soil humic acids the nitrogen question was settled differently. A number of investigators studying humic acids of various soils (Doyarenko, 1901; Kelley and Thompson, 1914; Shmuk, 1924, 1930; Hobson and Page, 1932) established a regularity in the presence of nitrogen in humic acids the content of which varied within 3–5 per cent. These

investigators also showed that during the acid hydrolysis of humic acids approximately a half of the total nitrogen passes into solution; in the composition of these hydrolysates, amides, mono- and diamino acids were found and the ratios between these groups were characteristic of typical animal and plant proteins (Table 10).

TABLE 10. THE FORMS OF NITROGEN IN HUMIC ACID FROM CHERNOZEM (Shmuk, 1924)

Forms of nitrogen	Water-soluble fraction of humic acid		Fraction of humic acid insoluble in water	
	As % of total N	As % of soluble N	As % of total N	As % of soluble N
Nitrogen of amides	10.1	23.25	11.25	25.35
Nitrogen of monoamino acids	28.0	65.88	28.75	64.79
Nitrogen of diamino acids	4.7	10.85	4.37	9.86
Nitrogen insoluble	57.2	—	55.63	—

Shmuk hydrolysed humic acid with 25 per cent H_2SO_4 as recommended for proteins (Hausman–Osborne method), and found that the ratio amides : monoamino acids : diamino acids in the hydrolysate was 25 : 65 : 10; according to numerous data, a similar ratio is characteristic of plant and animal proteins.

Suzuki (1906–1908), Robinson (1911), Shmuk (1924) and others, isolated and identified alanine, amino-valeric acid, aspartic acid, glutamic acid, leucine, an amino acid of the aromatic series (tyrosine), heterocyclic products of protein decomposition (proline and histidine) and other compounds among the products of hydrolysis. During alkali fusion Shmuk found indole, skatole, pyrrole and their derivatives in the humic acid from chernozem.

The earlier data on the composition of amino acids of humic acids have recently been confirmed by the use of paper chromatography (Bremner, 1954, 1955; Sowden and Parker, 1953; Stevenson, Marks, Varner and Martin, 1952; Pavel, Koloušek and Šmatlák, 1954; Okuda and Hori, 1954, 1955; Hayashi and Nagai, 1956; Kononova and Aleksandrova, 1956; Muresanu, 1960; and others). Purines and pyrimidines, which are derivatives of nucleic acids, were also found (Anderson, 1958, 1961).

During the hydrolysis of humic acids by means of 6 N HCl a large part of the nitrogen passes into solution; in addition, various investigators have found in the hydrolysate 22 amino acids, with a distribution which

is fairly similar in humic acids from various soils (this can be seen from Fig. 5). It was shown that a large part of the nitrogen passes into solution even during a hydrolysis with dilute acids (e.g. 5 per cent HCl, see table 11). Clearly, part of the nitrogen is represented not by typical proteins but by simpler forms. It was found, too, that the capacity of the nitrogen for hydrolysis with 6 N HCl differs with different humic acids: in humic acids from chernozem only 44 per cent of the total amount of nitrogen passes into solution, while in humic acids from podzolic soil, 73 per cent passes into solution (Kononova and Aleksandrva, 1956). The residue after hydrolysis contains cyclic (indolic) forms of nitrogen (Flaid and Breyhan, 1956).

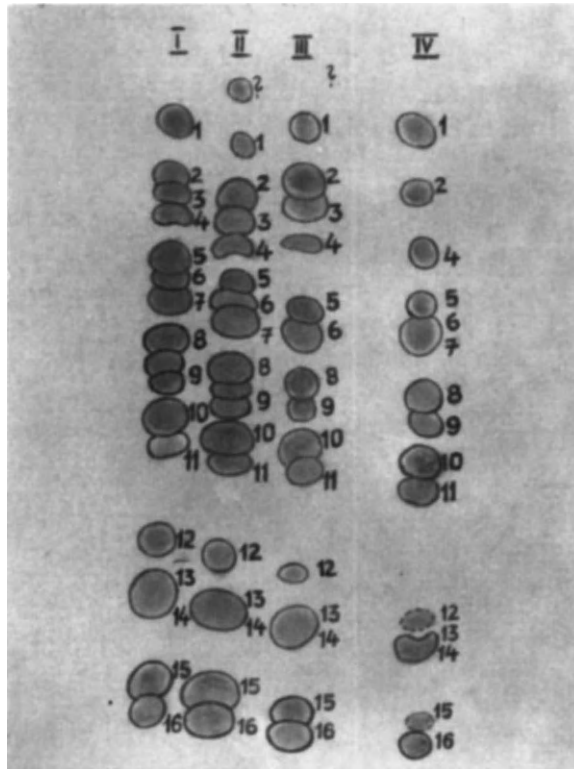


FIG. 5. Chromatograms of hydrolysates of humus substances
(Hydrolysis with 6 N HCl).

I. Newly formed humus substances; II. Humic acids from podzolic soils; III. Humic acids from chernozem soil; IV. Fulvic acids. 1. Cystine; 2. Lysine; 3. Histidine; 4. Arginine; 5. Aspartic acid; 6. Glycine; 7. Serine; 8. Glutamic acid; 9. Threonine; 10. Alanine; 11. Proline; 12. Tyrosine; 13. Valine; 14. Methionine; 15. Phenylalanine; 16. Leucine.

In spite of the fact that the ratio of amino acids and their composition in humic acids differ little from the corresponding values for proteins of plant and animal residues, the view that nitrogenous compounds of the latter are present in the humic-acid molecule in an unchanged form is hard to accept. Organic residues entering the soil are decomposed by micro-organisms, the decomposition of the original organic compounds being accompanied by the new formation (resynthesis) of microbial plasma, which consists of 80–90 per cent proteinaceous substances. From the works of Kostychev (1886), who first demonstrated the conversion of the nitrogen of plant residues into microbial plasma, and from the works of numerous investigators who have since developed this idea, it has become clear that the nitrogen present in humic acids is of microbial origin.

There is no doubt, however, that the protein of microbial plasma is present in humic acid in a much modified form; this can be seen from the results of humic-acid hydrolysis. Thus, in the investigations on the form of nitrogen in humic acids mentioned above (Doyarenko, Kelley, Shmuk and others), hydrolysis was carried out with 25 per cent H_2SO_4 for twenty-four hours, as recommended for typical proteins; this resulted in 60 per cent of the total nitrogen passing into solution. However, Dragunov showed, firstly for peat humic acids (1934, 1935, 1936) and secondly for soil humic acids (1948, 1950), that the same amount of nitrogen passes into solution during a much milder hydrolysis with 5 per cent HCl for $2\frac{1}{2}$ hours. Therefore, the hydrolysable part of the nitrogen of humic acids is represented, not by typical protein, but apparently by products of fairly advanced decomposition which are in the form of an unstable linkage with the humic-acid ring. Otherwise the conversion of nitrogen into a soluble form by the action of the dilute acid would not take place so readily and in so short a time.

The unhydrolysable part of the nitrogen of humic acids, which amounts to 40–50 per cent of the total amount, is generally thought to be represented by more oxidized nitrogenous forms occurring in a stable linkage with the remaining part of the humic acid molecule.

Hobson and Page (1932), using various methods of humic-acid purification—washing, reprecipitation, dissolving in alcohol, ultrafiltration—found that during these treatments humic acid lost approximately 43 per cent of its total nitrogen.

Moreover, with the action of the proteolytic enzymes trypsin and pepsin on the purified humic acid, a further 18 per cent passed into solution during four days. This investigation showed therefore that the amount of nitrogen with unstable forms of linkage was about 60 per cent of the

TABLE 11. THE HYDROLYSABLE FORMS OF NITROGEN IN HUMIC ACIDS

Humic acid	Nitrogen of humic acid (%)	Nitrogen of the hydrolysate		Method of hydrolysis	Author
		amount	% of total N		
From peat	1.72	0.89	51.8	5% HCl for 2½ hrs	Dragunov and co-workers, 1948
From medium podzolic soil, Moscow region	4.85	2.43	50.0	5% HCl for 2½ hrs	
From chernozem, Kursk region	4.04	2.17	53.8	5% HCl for 2½ hrs	
From chernozem, Kursk region	4.10	2.37	57.8	25% H ₂ SO ₄ for 24 hrs	Bel'chikova

total amount present in the humic acid. When humic acids from soils, peats and lignites were subjected to proteolysis by papain, Scharpenseel and Krausse (1962) found that at least one third of the amino acids had peptide and amide bonds.

Undoubtedly, the availability of humic acids to micro-organisms, and subsequently to plants, depends on the form of nitrogen linkage in the humic acids. This important fact should be taken into consideration when estimating the nitrogen reserves of soils (see Chapter 4).

The structure of the humic-acid molecule. From the data at present available it has been established that the humic-acid molecule consists of (a) an aromatic ring (b) nitrogen-containing compounds in cyclic forms and in the form of peripheral chains and (c) possible reducing substances. The humic-acid molecule has, therefore, a complex structure.

In considering humic acids as high-molecular-weight compounds, it should be recognized that the humic-acid molecule is a product of the condensation of aromatic compounds with products of protein decomposition, with the possible participation of substances of carbohydrate nature. As the formation of humic acids is due to the condensation of various substances Dragunov (1948) proposes the name of heteropolycondensates for them. On the basis of experimental data on the elementary composition, the presence of functional groups, the amount of hydrolysable and unhydrolysable forms of nitrogen, the amount of reducing substances and the nature of the aromatic ring of humic acid from chernozem, Dragunov presented a scheme for the structure of the latter as illustrated in Fig. 6.

Without discussing this scheme in detail we would point out that for soil humic acid it seems more accurate than Fuchs's scheme since it repre-

acid molecule agrees in principle with the ideas of many contemporary investigators, who look upon humic acids as products of the condensation of aromatic compounds of polyphenol type with nitrogen-containing compounds.

However, as with any scheme, it is only approximate and needs more precise development. The amount of "structural units" and their arrangement in the molecule have not yet been elucidated. It may be assumed that the primary condensates formed from "structural units" are monomers which combine to form polymers (Thiele and Kettner, 1953). The linkages between "structural units" and monomers are established by oxygen bridges and also by way of $-\text{NH}-$, $=\text{N}-$, $-\text{S}-$, $-\text{CH}_2-$ and other groups. The presence of these bridges gives the humic-acid molecule a loose structure.

Humic acids do not possess a clear, crystalline structure; this has given rise to contradictory interpretations. Sedletskii (1935, 1942), Jodl (1941, 1942) and also Gemmerling and Zyrin (1942) found by means of X-ray analysis that humic acids from soils and peats give 2-3 diffuse X-ray diffraction lines. They regard these results as evidence of the crystalline structure of humic acids.

Gorbulnov (1947), however, from his studies of soil humic acids, concludes that these diffuse diffraction lines are due to intra-molecular diffraction and he therefore believes that humic acids have an amorphous structure. Similar ideas were expressed by Jung (1946), Kasatochkin, Kukhareenko, Zolotarevskaya and Razumova (1950), Flaig and Beutelspacher (1951) and Beutelspacher (1952).

The degree of orderly arrangement of humic-acid molecules depends on their origin. Kukhareenko (1955) noticed that during the process of coal formation the interference lines become more distinct on passing from "less mature" materials (brown coal) to more "mature" ones (weathered coal).

We observed a similar phenomenon during a comparative study of humic acids isolated from different soils (Kononova, 1956); the diffuse diffraction lines were more distinct with humic acids from chernozems than with humic acids from podzolic soils and krasnozems.

Of special interest are electron-microscope studies of humic acids. Zolotarevskaya (1951), Flaig and Beutelspacher (1951, 1954), Beutelspacher (1952) and Kukhareenko (1953b, 1955) conclude that humic acids consist of tiny spherical particles capable of uniting into chains and of forming racemose aggregates (Figs. 8 and 9). Under certain conditions (e.g. at low pH) these particles are liable to undergo coacervation. The

aggregation of humic acids in an acid medium takes place through hydrogen bondings (Flaig, 1958).

On the basis of viscosity measurements, from determinations of the diffusion coefficient and from electron-microscope observations, Beutelspacher (1952), Flaig and Beutelspacher (1954) conclude that humic acids consist of sphero-colloids. However, as mentioned earlier, the molecules of humic acid do not have a compact structure.

The molecular weights of humic acids have not yet been established beyond question. Results from osmometry (Zamek, Arnold), cryoscopy (Fuchs, Tissen, Kürschner), viscometry and diffusion measurements (data on this problem are collected in the monograph by Scheffer and Ulrich, 1960, p. 54) give molecular weights for humic acids ranging from 700 to 1400, values on the whole similar to those (*c.* 1300) obtained at one time by Oden. However, Flaig and Beutelspacher, using the ultracentrifuge, found molecular weights in the range 30,000–50,000 (see Flaig, 1958). Mehta, Dubach and Deuel (1963) using the method of filtering on Sephadex with different pore sizes, have established that the molecular weight of various fractions of humic acids varies from 2000 to over 100,000.

There is a wide variation in the equivalent weights of different humic acids (Kukhareenko, 1950; Schnitzer and Desjardins, 1962; Pommer and Breger, 1960). Thus Schnitzer and Desjardins, determining the molecular weight of organic matter from podzol A_o and B_h horizons by the freezing point depression method, found values 1684 and 669 respectively. Equivalent weights were 165 for the A_o organic matter and 76 for B_h , so that the ratio of molecular weight to equivalent weight was 10 for organic matter from the A_o horizon and 9 for the horizon B_h . These ratios were equal to the sum carboxylic and phenolic groups.

The study of the chemical nature and structure of humic acids is of the utmost importance in discovering their role in soil processes. The presence of functional groups—carboxyl and phenolic hydroxyl—determines both the exchange capacity and the types of compound formed with metals (in particular, the tendency to complex formation). As is now becoming clear, the shape of the molecule of organic substances is of great importance in the formation of soil structure: substances with molecules of linear form (e.g. polyuronic acids) participate in this process more actively than humic acids of spherical form.

The fact that humic-acid molecules are not compact but have a loose (spongy) structure with a large number of internal spaces is of great importance in soil processes. These characteristics of the structure determine the water-holding capacity and the sorptive properties of humic acids

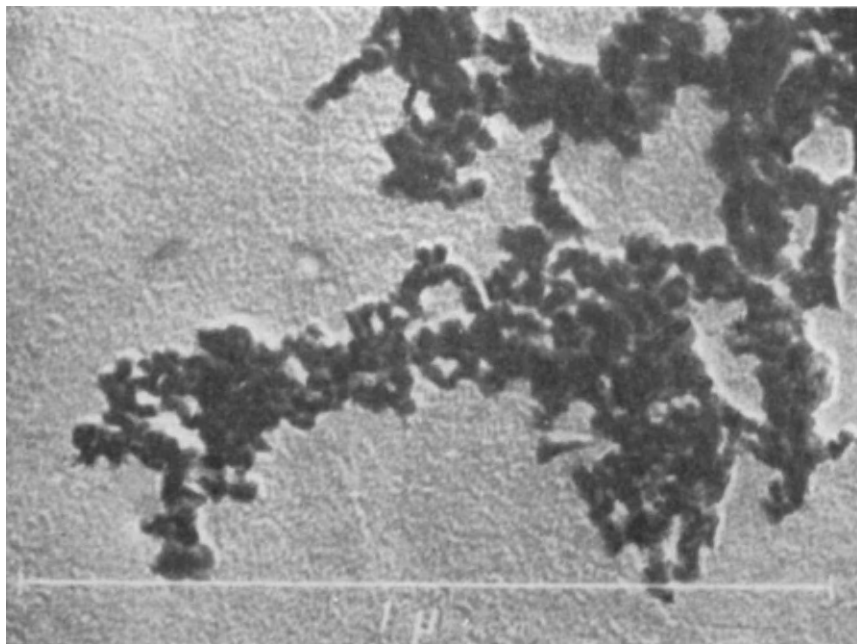


FIG. 8. Electron-microscope photograph of humic acids from chernozem at pH 3.8.
($\times 105,000$) (Beutelspacher, 1955).

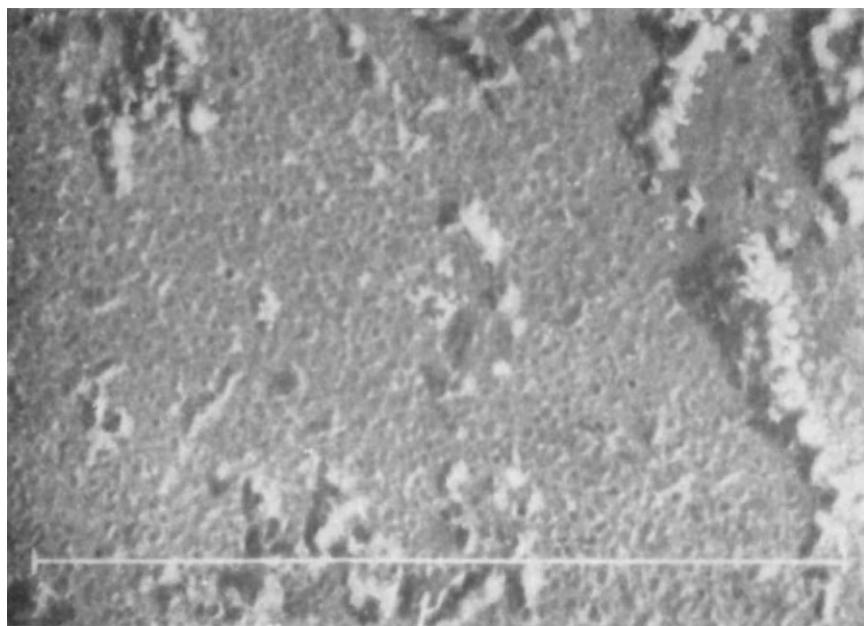


FIG. 9. Electron-microscope photograph of sodium humate from chernozem.
($\times 105,000$) (Beutelspacher, 1955).

to a considerable degree. A number of investigations of humic acids by X-ray diffraction (Kasatochkin, 1951; 1953; Kasatochkin and Zil'berbrand, 1956; Kononova, 1956; Kumada, 1955, 1956, 1958; Kobo and Tatsukawa, 1959) have shown that they possess an aromatic net, characterized by the interference band 002, and peripheral aliphatic chains characterized by the band " γ ". Furthermore, as humic acids increase in "maturity" their aromatic nature becomes increasingly clear.

A number of important properties of humic acids—the rate of their exchange reactions, the mobility of nitrogen and also their hydrophilic properties—depend on the ratio between aromatic and aliphatic structures in the molecules. Apparently, the pronounced hydrophilic nature of humic acids from podzolic soils is explained by the predominance of the aliphatic structure (possessing hydrophilic properties). On the contrary, humic acids from chernozem, which have a clearly expressed aromatic ring (with hydrophobic properties), are less hydrophilic. This explains the important fact that, compared with humic acids from chernozems, humic acids from soils of the podzolic series possess a high capacity for peptization, are more stable towards electrolytes and are extremely mobile.

We shall return to the problem of the regular differences in the nature and properties of humic acids of different soils at the end of this chapter and also in Chapter 6.

Humins of soil humus

Humus substances not extracted from decalcified soil during treatment with alkali solutions are placed in the humin group. According to Sprengel, who was the first to draw attention to this group of substances, they occupy a position intermediate between humic acids and coal, and for this reason were named "humus coal". Later, Berzelius replaced this rather unsatisfactory term by "humin" and Mulder introduced the term "ulmin" for the insoluble form of ulmic acid.

Later investigators were not unanimous in their opinion about this group of substances. Thus, according to Odén (1919), humus substances unextractable from peat are anhydrides of humic acid and he uses Sprengel's term "humus coal" for them. The opposite view was expressed by Shmuk (1930), who denied the existence of humins as a separate group of humus substances. He considered that soil humins were components of plant residues occurring in various stages of humification.

According to Williams, humin and ulmin are denatured forms of humic and ulmic acids. They are converted into a denatured form as a result

of desiccation or freezing. Williams linked an important role of humus substances—that of importing stability to soil crumbs (saturated with highly dispersed solutions of ulmic and humic acids)—with the conversion of the humic acids into humins. Denaturation is an irreversible process, and therefore the conversion of humin and ulmin into a soluble state does not restore the properties characteristic of active humus. In this connexion, Williams pointed out that humus substances can only participate once in the creation of a stable soil structure.

The investigators who studied brown coal and mineral coal associated humin formation with an alteration in the chemical nature of the humic acid—dehydration, condensation, polymerization and diminution in the number of functional groups (Fuchs, 1931).

The loss in humic acids of the capacity for dissolving in alkali under soil conditions is due not so much to an alteration in their nature as to the form of the linkage existing between them and the mineral part of the soil. During recent years, a number of investigators (Tyurin and Gutkina, 1940; Khan, 1945; Zyrin, 1948; Naidenova, 1951) have turned their attention to this subject and their works have made the conception of humin much clearer.

Tyurin and Gutkina (1940), during studies of the nature of humin of chernozem, first removed humic acids by means of 0.1 N NaOH after preliminary decalcification of the soil; the soil residue was then subjected to: (1) short acidification with 5 N HNO₃ (according to Fuchs) to convert humins into a soluble state; (2) treatment with HF to release the humin group from its combination with silicates; and (3) treatment with acetyl bromide to remove the unhumified fraction. As a result of these treatments, a part of the humus substances present in the composition of humin acquired the capacity for dissolving in alkali.

A study of the substances passing into alkali solution during these operations led Tyurin and Gutkina to the conclusion that the humins of chernozem represent a complex of substances similar to that isolated from decalcified soil by treatment with alkali solution; it consists of humic acids and fulvic acids. Tyurin revealed a homogeneity in the whole of the humin fraction by repeated treatment with 5 N HNO₃ (according to Fuchs) followed each time by treatment with 0.1 N alkali. The humic acids obtained in this way all have the same carbon content.

An interesting observation was that humic acids from the humin fraction contained a somewhat lower percentage of carbon and a higher percentage of oxygen and hydrogen than did humic acids extracted from decalcified soil; it was also observed that they had a lower absorption

capacity. This suggests that humic acids from soil humins are of simpler nature than those extracted from soil after decalcification (Table 12).

TABLE 12. CHARACTERISTICS OF HUMIC ACIDS ISOLATED FROM DECALCIFIED SOIL AND FROM THE HUMIN FRACTION (Tyurin and Gutkina, 1940)

Humic acids	Elementary composition (%)				Absorption capacity (Ca acetate) m eq per 100 g substance	Equivalent weight
	C	O	H	N		
From decalcified soil	62.78	30.21	3.53	3.48	459.3	218
Isolated from humin fraction:						
after treatment with 5 N HNO ₃	58.92	30.58	4.55	5.95	365.47	274
after treatment with 5 N H ₂ SO ₄	57.83	32.63	4.41	5.13	379.2	264

Similar results were obtained by Khan (1945) during investigations on the humins of podzolic soil. After decalcification of the soil, Khan first removed humic acids soluble in alkali, then employed alternate treatment of the soil residue with H₂SO₄ at increasing concentrations from 7 to 25 per cent (with slight heating) with subsequent isolation of the humic acids with 0.1 N NaOH solution. In this way, he succeeded in bringing into solution up to 88 per cent of all humins; the humic acids isolated in this way (by both Tyurin and Gutkina) contained a lower percentage of carbon and a higher percentage of hydrogen and oxygen than did humic acids from decalcified soil (Table 13).

Z̄yrin (1948), who studied the humins of podzolic and chernozem soil, was successful in bringing practically all humins into solution by carrying out a number of alternate treatments, first with acid, then with 0.1 N NaOH. In another experiment Z̄yrin treated soil with H₂SO₄ and HF to decompose the mineral constituents; after this treatment, nearly all of the humins passed into alkali solution. The humic acids obtained in this way were similar in elementary composition to the humic acids isolated from decalcified soil (Table 14).

From an examination of the works of Tyurin and Gutkina and those of Khan and Z̄yrin, it can be seen that the humins of soil humus are humic acids generally resembling fairly closely the humic acids isolated from the soil after decalcification; the loss of the capacity for dissolving

TABLE 13. ELEMENTARY COMPOSITION OF HUMIC ACIDS ISOLATED FROM DECALCIFIED SOIL AND FROM HUMIN FRACTIONS (Khan, 1945)

Humic acids	%C	%H	%O	%N
From medium podzolic soil:				
after decalcification	57.90	4.40	32.70	5.00
after treatment of the residue with 7% H ₂ SO ₄	55.00	5.56	35.69	3.83
after further treatment of the residue with 12.5% H ₂ SO ₄	53.00	5.52	37.59	3.89
after further treatment of the residue with 25% H ₂ SO ₄	52.20	5.13	38.43	4.10
From strongly podzolic soil:				
after decalcification	56.90	4.62	33.38	5.10
after treatment of the residue with 7% H ₂ SO ₄	53.60	5.40	37.20	3.80
after further treatment of the residue with 12.5% H ₂ SO ₄	53.20	5.82	36.97	4.01
after further treatment of the residue with 25% H ₂ SO ₄	54.29	5.87	35.89	3.95

TABLE 14. ELEMENTARY COMPOSITION OF HUMIC ACIDS ISOLATED FROM DECALCIFIED SOIL AND FROM THE HUMIN FRACTION BASED ON ASH-FREE MATERIAL DRIED AT 65° (Zyrin, 1948).

Humic acids	Investigated soils	%C	%H	%O	%N
From decalcified soil	chernozem (Kursk region)	59.89	3.28	34.18	2.55
From residue after treatment with HF and H ₂ SO ₄	chernozem (Kursk region)	60.28	3.58	34.87	1.27
From decalcified soil	medium podzolic soil (A ₁ horizon)	60.07	4.21	32.04	3.68
From residue after treatment with HF and H ₂ SO ₄		59.75	4.60	33.03	2.62

in alkali is attributed, not to an alteration in their nature, but to the firmness of the combination with the mineral part of the soil.

The firmness of the linkage depends to a large extent on the nature of the mineral constituents of the soil. Khan (1946, 1950, 1959), studying the absorption of neutral ammonium humate by various minerals, showed that the linkage was most stable where there was an interaction between

humate and minerals of the montmorillonite type, when the absorption of humate takes place apparently in the mineral lattice (askanite and gumbrin). In the case of kaolin, orthoclase, feldspar and microcline, humic-acid molecules are adsorbed by the surface of the crystal; in this form the linkage between humic acids and minerals is easily destroyed by treatment with 0.1 N NaOH. The intensity of humate absorption depends on the degree of dispersion of the minerals, on the nature of the absorbed bases and on various other factors.

However, the nature of the humic acids themselves appears to be of importance in determining the degree of stability of their linkage with the mineral part of the soil. Attention is drawn to the fact that humic acids isolated from the humin fraction are characterized by a lower percentage of carbon, a higher percentage of hydrogen and oxygen and also by the fact that they are less oxidized (with respect to the O/H ratio) than humic acids isolated from decalcified soil (Tyurin and Gutkina, 1940; Khan, 1945). These characteristics seem to indicate the relatively simple structure of the humic-acid molecules of humins.

Being high-molecular-weight compounds, humic acids are represented by molecules of various sizes. Obviously, the smaller the molecule the more stable is the form of linkage between humic acids and the mineral part of the soil. Sakun's work (1942) does in fact show that low-molecular-weight humic acids with a molecule size of 2×10^{-7} , i.e. occurring in the form of true solutions, interact most actively with clays. This is in agreement with the results obtained by Tyurin and Gutkina and by Khan, indicating the relatively simple nature of humic acids from humins, which, in our opinion, is not coincidental.

It is clear from these remarks that the isolation of humins as a separate group, which is associated with the idea of the occurrence of fundamental changes in the chemical nature of humic acids (the loss of functional groups, dehydration, etc.) during the formation of mineral coal, has no foundation with regard to soil humus.

In the majority of soils, the humin group is represented mainly by humic acids; their loss of the capacity for dissolving in alkali solutions is due mainly to their stable linkage with the mineral part of the soil.

In some soils, the group of organic substances termed humin is of a peculiar nature; in peat soils, for instance, it is represented by incompletely humified plant residues, as was shown by Shmuk (1930). According to our investigations (1943), the organic substances of the humin of serozem are represented by stable forms of protein (melanines), a source of which is microbial plasma, which is abundant in soils of this type.

In soils, the humin group may be partly represented by carbonized plant residues whose presence is not always the result of forest burning; small pieces of carbon are present in certain amounts in all soils, particularly in moist meadow soils with restricted aeration. Under such conditions a part of the plant residues is subjected to carbonization; those residues insoluble in alkali are included in the humin group (Najmr, 1960).

Besides participating in the formation of a water-stable structure, this group of humus substances is important because it constitutes a concentration of considerable amounts of nitrogen, phosphorus, sulphur and other elements, forming a reserve which is gradually drawn into cycles of mineralization and mobilized for plant nutrition.

Fulvic (crenic and apocrenic) acids

Perhaps no other group of humus substances has aroused so much controversy as the group of crenic and apocrenic acids. Crenic acid or "spring" acid was first isolated by Berzelius from the water of a mineral spring and this explains its name. Berzelius showed that, during atmospheric oxidation, crenic acid is converted into brown, sparingly soluble substances superficially resembling humic acids, which he termed sedimentary spring acid or apocrenic acid. Crenic and apocrenic acids were also isolated by Berzelius from the water extracts of humus-rich soil, from bog-ores and, by German and Mulder, from various soils and peats. In the last case, crenic and apocrenic acids were extracted, together with humic acids, by treatment with alkali solutions, and their isolation from the acid solution after the precipitation of humic acids was brought about in the form of copper salts by treatment with copper acetate; in acid conditions apocrenic acid precipitated out, and during subsequent neutralization of the filtrate with ammonium carbonate crenic acid was precipitated. The copper salts of crenic and apocrenic acids were then decomposed with hydrogen sulphide and, after filtration, solutions of the acids in a free state were evaporated to dryness in a vacuum. Crenic acid, according to Berzelius's description, has a yellowish colour, is amorphous and has a sharp taste; apocrenic acid is of brownish colour. Both possess acid properties.

German and Mulder, from a determination of the elementary composition of crenic and apocrenic acid, found that they contained a lower percentage of carbon and a higher percentage of oxygen than did humic acids and ulmic acids. On the basis of analytical data, structural formulae for crenic and apocrenic acids were proposed. This accorded with the ideas of

the period, which recognized crenic and apocrenic acids as chemically individual compounds (Table 15).

TABLE 15. ELEMENTARY COMPOSITION OF HUMIC ACIDS ACCORDING TO MULDER
(see Tyurin, 1940)

Name of acid	%C	%H	%O	%N
Ulmic acid from peat (mean of two analyses)	62.02	4.65	33.48	not det'd
Humic acid from different soils (mean of five analyses)	57.20	4.80	34.10	3.9
Apocrenic acid (mean of four analyses)	48.80	4.00	44.60	2.5
Crenic acid (mean of three analyses)	44.80	5.30	47.90	1.9

Berzelius made comprehensive studies of the K, Na, NH_4 , Ba, Ca, Mg, Al, Mn, Fe^{2+} and Fe^{3+} salts of crenic and apocrenic acids (colour, solubility in water, ammonia and other solvents). The tendency for the formation of salt-like compounds with a number of elements, particularly with Ca, Mg, Al and Fe, and the ready solubility of these compounds led to the assumption that they play an important part in soil formation.

Sibirtsev (1900–1901) was the first to indicate that the development of the soil-forming process is closely associated with the accumulation in the soil of crenic and apocrenic acids, with the decomposition of silicates (in which these acids participate) and the consequent formation of insoluble silica, and also with the easy mobility of the crenates and apocrenates formed and their removal from the upper part of the soil profile. Even in Academician Williams's earlier works (1902) there are similar indications, which he later developed and put forward as the basis of his theory of the podzol-forming process.

From the beginning of the present century, however, the existence of crenic and apocrenic acids has been open to question. Scepticism towards the existence of this group of substances became particularly noticeable after the appearance of the works of Schreiner and Shorey, who isolated a number of low-molecular-weight substances of a non-specific nature — organic acids, various products of protein decomposition, pentosans and other compounds — from the acid solution obtained after the precipitation

of humic acids (i.e. from the fraction containing crenic and apocrenic acids).

While there is justification at present for believing that crenic and apocrenic acids, like humic acids, are complex substances of synthetic nature, it is clear that the chemically individual compounds detected by Schreiner and Shorey in acid solution may, in part, represent the components of molecules of crenic and apocrenic acids. At a time when humus substances were still regarded as chemically individual compounds, the hypothesis of the existence of crenic and apocrenic acids as a specific group of substances was undermined by Schreiner and Shorey's investigations.

However, at about the same time, there was another view on this group of substances which owed its origin to Odén (1919). Odén introduced the new term "fulvic acids" for the group of humus substances occurring in peat waters. He described these substances as compounds of high molecular weight characterized by a reduced (less than 55 per cent) carbon content and high solubility in water, alcohol and alkali; their salts are also readily soluble in water. At low concentrations these substances are slightly yellow in colour; in concentrated solutions they are orange-yellow resembling potassium dichromate solution. This was the basis for the introduction of the term "fulvic acids" (*fulvus* = yellow).

Odén considered the term "fulvic acids" to be a group concept on the assumption that these acids were analogous to the crenic and apocrenic acids of Berzelius. However, it must be mentioned that Berzelius's "crenic" and "apocrenic" acids included only those compounds isolated from spring waters and from water-extracts of soils.

Not only did the introduction by Odén of a new term fail to increase the precision of previous ideas on crenic and apocrenic acids, but during subsequent years it actually gave rise to a confusion of views. Some investigators continued to study this group of substances according to the ideas of Schreiner and Shorey, isolating various organic substances from the acid solution after the precipitation of humic acids. Thus, Hobson and Page (1932) found peptides, amide-nitrogen, free amino acids and other compounds in the acid solution and this on first appearance seemed to confirm Schreiner and Shorey's point of view that crenic and apocrenic acids are a mixture of substances of non-specific nature. On the other hand, Tyurin (1940) in his scheme for the determination of the composition of humus includes in his conception of "fulvic acids" (regarding the latter as analogous to crenic and apocrenic acids) all the organic substances remaining in the acid solution after the precipitation of humic acids. For the purpose of studying the nature of fulvic acids, Tyurin isolated them from

acid solutions in the form of ammonium salts. Finally, according to some investigators (Stadnikov, 1932a, b), fulvic acids are humic acids capable of dissolving in water.

Scepticism towards the existence of this group of substances was the reason for the decreased attention paid to them and, as a result, this important group of humus substances has up to the present been insufficiently studied.

Tyurin (1940b) resumed the study of crenic and apocrenic acids, taking their important role in soil formation into consideration. He carried out the isolation of these substances as follows: after preliminary decalcification and extraction of the soil with an ethanol-benzene mixture, humic acids were extracted with 1 per cent ammonia solution containing a small amount of ammonium carbonate. The solutions of humus substances obtained were filtered through membrane-filters and evaporated to dryness in porcelain dishes on a gently boiling water-bath to remove free ammonia and ammonium carbonate. The dry residue was dissolved in hot water and humic acids were precipitated from the solution by the addition of 1.0 N H_2SO_4 . After removing the precipitate the acid solution was treated with a fine suspension of carefully washed barium carbonate to bind SO_4^{--} and convert fulvic acids into barium salts. The latter were then decomposed by means of ammonium carbonate. The resulting solution of ammonium salts of crenic and apocrenic acids was then made up to the required volume and from this solution samples were taken for analysis.

Tyurin's data on the elementary composition of fulvic acids were similar to the data obtained by Mulder for crenic acid (see Tables 15 and 16). Hydrolysis of fulvic acids with 5 per cent H_2SO_4 showed the presence in fulvic acids of 20–25 per cent reducing substances, and boiling with 12 per cent HCl liberated furfural and CO_2 in amounts corresponding to 5–10 per cent pentosans and 5–20 per cent uronic anhydride. Fulvic acids showed the ability to enter into exchange reactions: the capacity for NH_4 absorption was 318.6 m eq for fulvic acids from podzolic soil and 324 m eq per 100 g substance for those from chernozem.

Tyurin, as a result of his investigations, concluded that "fulvic acids of soil humus represent hydroxycarboxylic acids of high molecular weight (containing nitrogen) with an equivalent weight (in relation to NH_3) of about 300, distinguishable from the humic-acid group by their light colour, considerably lower carbon content, solubility in water and in mineral acids, and much greater capacity for acid hydrolysis" (1940, p. 35).

Tyurin attributed the regularity of the isolation of fulvic acids with humic acids and their contradictory behaviour (their capacity for dissolving

in water and acids on the one hand and their unextractability from soil with either water or acids on the other) to the occurrence of fulvic acids and humic acids in the form of compounds of complex-ester type. These esters are decomposed by alkalis with the formation of humic acids and fulvic acids characterized by greater solubility in water and acid solutions. Tyurin was of the opinion that the low solubility of fulvic acids in water was in some cases due to their combination with sesquioxides.

An example of the latter is found in the humus-illuvial horizon of podzolic soils, the fulvic acids of which were studied by Ponomareva (1947, 1949). She investigated soil samples from the Kol'skii peninsula containing enormous accumulations of fulvic acids (up to 20–30 per cent of the weight of soil) in the form of specific compounds with hydrated sesquioxides leached mainly from the upper horizons. These complex compounds are soluble in cold dilute mineral acids (0.1–0.5 N), the extract having the colour of strong tea. After bringing the acid solution to a pH of about 5.0, nearly complete precipitation of fulvic acids and hydrated sesquioxides occurs as a complex organo-mineral gel, which passes into solution again when the pH is made slightly alkaline with NaOH.

From these samples Ponomareva isolated fulvic acids as their ammonium salts, by a method differing slightly from Tyurin's method already described. In elementary composition and absorption capacity the fulvic acids resemble those isolated by Tyurin from podzolic soil and chernozem; they also contain 10 per cent of reducing substances (Table 16).

During her study of fulvic acids from different soils Ponomareva (like Tyurin) showed that some variation in their nature occurred even in the

TABLE 16. ELEMENTARY COMPOSITION OF FULVIC ACIDS OF DIFFERENT ORIGIN

Fulvic acids	%C	%H	%O	%N	Absorption capacity (m eq/100 g substance)
From chernozem (Tyurin, 1940)	44.35	5.94	44.20	5.52*	324
From podzolic soil (Tyurin, 1940)	44.82	5.77	43.66	5.75*	318
From humus-illuvial horizon (Ponomareva, 1947)	45.3	5.0	48.6	1.1*	300

* The percentage of nitrogen in the first and second analysis is excessive due to the extraction being carried out with ammonia; in the third analysis Ponomareva introduced an appropriate correction factor.

same soil. This corresponded to some extent with Berzelius's ideas on the existence of two acids—crenic and apocrenic acids.

Both Tyurin and Ponomareva isolated fulvic acids as their ammonium salts and this obviously caused considerable difficulties during studies of their nature. Ponomareva's attempt to obtain fulvic acid in a free state by the electrodialysis of ammonium salts is therefore of interest. The electrodialysis was carried out with a constant potential of 80–100 mV until a negative reaction for OH^- was obtained in the external cathode cell (control sample contained phenolphthalein).

The electrodialysis method was also used by Ponomareva for the separation of humic acid and fulvic acids from mixed solutions of their ammonium salts. Due to the exchange of NH_4 for H^+ during the electrodialysis, humic acids coagulated and precipitated from the solution in the form of a gel, and fulvic acids remained in the cell in the form of a sol. The data on the elementary composition of fulvic acids isolated in a free state were identical with the data previously obtained for ammonium salts; their pH, however, was considerably lower (2.6–2.8 instead of 4.53) and the exchange absorption capacity was nearly twice as high (600–650 m eq instead of 300–350) and this, according to Ponomareva, indicates the high degree of dissociation and the large amount of active acid groups in fulvic acids compared with humic acids.

Ponomareva carried out a series of investigations on the interaction of fulvic acids with NH_4OH , NaOH , $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$, on the solubility of these organo-mineral compounds and on the explanation of the conditions governing their migration in the soil profile. Her results are extremely important for an understanding of the process of podzol formation.

We turn now to the work of Forsyth (1947) also dealing with an investigation of the nature of soil fulvic acids. The objects of his study were deep-humus soils with a cover of heather and Scots pine, gardeners' "turf" soil and Sphagnum peat. The presence of a large amount of partly decomposed plant residues in the investigated samples would explain the great variety of substances found by Forsyth in an acid solution after precipitation of the humic acids. The humic acids were extracted by means of cold 0.5 N NaOH followed by precipitation of the humic acids with HCl at pH 2.5–3.0. The acid solution obtained after precipitation of the humic acids was filtered through animal charcoal; a large part (up to 90 per cent) of the organic substances remained on the charcoal and was eluted by means of various solvents. Forsyth isolated four fractions.

The first fraction (A) consisted of organic substances passing through

the charcoal; nitrogen-containing compounds and reducing substances were detected after evaporation.

The second fraction (B) contained organic substances eluted from the charcoal with acetone containing 10 per cent water. After removing the acetone and subsequent purification of this fraction, carbohydrates giving a positive Molisch reaction and positive reactions also with phloroglucinol and orcinol were detected. Phenol-type substances and glycosides were also detected in this fraction by the appearance of a green coloration with FeCl_3 . Forsyth regarded the latter substances as intermediates in the formation of humic acids.

The third fraction (C), washed from the charcoal with distilled water, gave, on the addition of acetone, a flocculent precipitate, which, after reprecipitation and purification, showed a positive reaction for glucose and glucuronic acid.

Finally, the fourth fraction (D) represented, according to Forsyth, strictly fulvic acids. They were eluted from the charcoal with 0.5 N NaOH solution; the solution had a deep wine-red colour. To obtain the fulvic acids in a free state, the alkaline solution was dialysed to pH 8–9 and then electro-dialysed in a 3-cell dialyser using a current of up to 2 amp.

A large part of the organic substances was obtained as a dark precipitate on the anode; this was filtered, dried *in vacuo* and, after grinding, the free fulvic acids were obtained as a brown powder. The elementary composition of the latter was similar to that of apocrenic acids:

Fulvic acids	%C	%H	%N	%Ash
From heather raw humus	48.44	5.49	4.17	2.16
From gardeners' "turf" soil	47.25	5.61	5.87	4.10

Although fulvic acids were found to be rich in nitrogen, the reaction for protein was, however, negative; consequently, their nitrogen must occur in the form of complex compounds. Fulvic acids showed a positive reaction with phloroglucinol and with orcinol (indicating pentosans). They contained considerable amounts of phosphorus, showed the properties of acids, were soluble in alkalis and were precipitated from solution by alcohol, lead acetate, and also—after neutralization of the solution—by aluminium salts.

A further study of the chemical nature of fulvic acids can be found in recent work. One difficulty in solving the problem is that many authors

even at the present time include in the concept "fulvic acids" all organic substances in the acid solution left after humic acids have been precipitated from extracts. This group of substances is very diverse in composition; besides strictly fulvic acids, carbohydrates, glucosides, substances of phenolic nature, uronic acids and nitrogen-containing organic acids were found in this group (Forsyth, 1947; Dragunov and Vysotskaya, 1953; Schlichting, 1953a; Dubach, Zweifel, Bach and Deuel, 1955).

Especially interesting are the investigations of isolated fulvic acid preparations. This work is far from complete, yet it shows the complex structure of fulvic acids. Drozdova (1955) isolated fulvic acids from peat and a podzolic soil, and by chromatography on coal, detected compounds of an aromatic nature in their composition (phenolic glucosides, and an acid of quinoid nature). By a similar chromatographic method using activated coal, Kukharensko and Vvedenskaya (1959) studied the nature of fulvic acids isolated from brown coal and peat. They concluded that these acids have an aromatic structure containing methoxyl, carboxyl and phenolic hydroxyl groups — in other words the very same groups that are characteristic of humic acids. Schnitzer and Wright (1950, 1961) studying the organic matter of the podzolic B horizon, which was mainly represented by fulvic acids, obtained similar results.

The ability of fulvic acids for taking part in exchange reactions is explained by the presence of carboxyl and phenolic groups. As can be seen from Fig. 2, the potentiometric titration curves are similar to those for humic acids and are characteristic of polybasic organic acids; the equivalence point occurs at pH 8–9.

Investigations by infra-red spectroscopy have shown that components of an aromatic nature are present in fulvic acids (Kasatochkin and co-workers, 1956, 1958; Kobo and Tatsukawa, 1959; Schnitzer, Shearer and Wright, 1959).

The spectrum of fulvic acid from a sod-podzolic soil is given in Fig. 4b; it has features in common with the spectra of humic acids from chernozems. The band at 1697 cm^{-1} ($5.89\text{ }\mu$) corresponds with the vibration of carboxyl (carbonyl) $\text{C}=\text{O}$ in aliphatic and aromatic acids. The band at 1600 cm^{-1} ($6.25\text{ }\mu$) characterizes the stretching vibration of the conjugated carbon double bonds in aromatic structures; in consequence it can be assumed that there is an aromatic carbon net in fulvic acids. The presence of CH_3 and CH_2 of aliphatic groups is shown by the band at 1388 cm^{-1} ($7.21\text{ }\mu$). Near 1128 cm^{-1} ($8.87\text{ }\mu$) and 1010 cm^{-1} ($9.9\text{ }\mu$) are situated bands characteristic of $\text{C}-\text{O}$ stretching vibration or $\text{O}-\text{H}$ bending vibration (alcohols, acids, ethers or esters). However, X-ray analysis shows that

the net of aromatic carbon in fulvic acids is very weakly expressed, and side radicals predominate.

The weak "aromatization" of fulvic acids is shown by their elementary composition (Table 20); the carbon percentage is much lower and the hydrogen percentage higher than in humic acids. Due to the weakly expressed aromatic structure, the ratio C:H is generally lower in fulvic acids than in humic acids.

Like humic acids, fulvic acids contain nitrogen. Bremner (1954) found that when fulvic acids were hydrolyzed with 6 N HCl, 20–30% of their nitrogen passed into the solution, in which he detected a large number of α -amino acids. Kononova and Aleksandrova (1956) used a similar method for hydrolyzing fulvic acids isolated from a chernozem soil and found the amino acid composition of hydrolyzate to be similar to that from humic acids (see Fig. 5). The high reactivity of nitrogen in fulvic acids is characteristic: hydrolysis with 2% HCl will dissolve 70% of the total nitrogen. Stevenson (1960a) showed that approximately 50% of the nitrogen in fulvic acid from a burozem was dissolved during acid and alkaline hydrolysis, 25% being amino acids and 10% amino sugars.

Consequently it follows that fulvic acids, having structural units similar to those in humic acids, are characterized by weakly expressed rings (aromatic carbon nets) and a predominance of side chains. Fulvic acids may therefore be considered the least "mature" representatives of the humic acid group.

Hymatomelanic acids

As is well known, the term "hymatomelanic acid" was introduced by Hoppe-Seyler (1889) for the substances extracted by alcohol from "raw" humic acid. According to Hoppe-Seyler, hymatomelanic acid is a chemically individual compound like the humic, ulmic, crenic and apocrenic acids of Sprengel, Berzelius, German, Mulder and other investigators. Later, the conventionality of the criterion—solubility in alcohol—by which Hoppe-Seyler differentiated these substances into a separate group of humus substances was elucidated. Odén regarded hymatomelanic acid as a compound possessing a number of specific characteristics (see Table 1) such as solubility in water, alcohol and alkali, carbon content (62 per cent), and equivalent weight (250). Odén also indicated the possibility of the formation of hymatomelanic acid from humic acid during alkaline hydrolysis.

A different point of view was expressed by Shmuk (1924, 1930). He denied the separate existence of hymatomelanic acids, regarding them as

a mixture of chemically individual compounds of the resin-acid type. Shmuk, in fact, isolated and identified in the alcohol-soluble fraction of humic acids from chernozem a number of resin acids differing in melting point and elementary composition. Finally, Fuchs (1931) regarded the hymatomelanic acid in coal as representing a product of humic-acid oxidation (dehydro-humic acids.)

In Tyurin's opinion, hymatomelanic acids represent a complex mixture of substances, which are humic-acid derivatives, some being more oxidized and others more reduced.

This group of substances has not attracted the attention of investigators in the field of study of soil humus during recent years. However, investigations in neighbouring disciplines (the chemistry of humus substances of peat and brown coal) have established their genetic similarity with humic acids (Kondrat'ev, 1940; Kukhareno, 1948).

On the basis of chemical investigations, Kukhareno came to the conclusion that hymatomelanic acids are apparently simpler forms of humic acid (Table 17).

TABLE 17. COMPARATIVE DATA ON THE CHEMICAL NATURE OF HUMIC AND HYMATOMELANIC ACIDS (Kukhareno, 1948)

Investigated acids	Carbon (%)	Hydrogen (%)	Formula of hymatomelanic acid	Molecular weight	Formula of humic acid	Author
From brown coal (Aleksandriisk)	68.99	6.58	$C_{11}H_{11}O_1 OCH_3$ (OH) ₁ OH* (COOH) ₂	772	$C_{71}H_{53}O_{13}(OH)_1$ OH* (COOH) ₃	Syskov and Kukhareno
From low-moor peat	65.38	6.98	$C_{11}H_{17}O_1 OCH_3$ (OH) ₃ OH* (COOH) ₂	792	—	
From high-moor peat	66.07	6.92	$C_{12}H_{17}O_1 OCH_3$ (OH) ₁ (COOH) ₂	804	$C_{63}H_{53}O_4 OCH_3$ (OH) ₁ (COOH) ₄	Kondrat'ev
From brown coal (Frlendorf)	62.80	7.02	$C_{39}H_{16}O_5 OCH_3$ (OH) ₂ OH* (COOH) ₃	800	$C_{72}H_{35}O_{10}(OH)_1$ OH* (COOH) ₄	Kukhareno

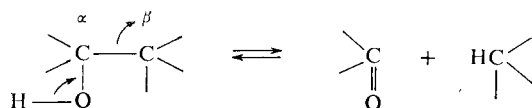
* Hydroxyl groups which react with BaO but not with Ca acetate.

Hymatomelanic acids contain methoxyl, carboxyl and hydroxyl groups; they have a characteristically high carbon content (more than 60%). The similarity of humic acids and hymatomelanic acids from mineral coals, as shown by their elementary composition and by the functional groups present (Table 18), has been demonstrated by Kukhareno and Ekaterinina (1960).

TABLE 18. COMPARATIVE CHARACTERISTICS OF HUMIC AND HYMATOMELANIC ACIDS FROM WEATHERED COAL (KUZNETSKII BASIN)
(Kukhareno and Ekaterinina, 1960)

Extraction solvent	Acid	Elementary composition %			Group, m eq per g		
		C	H	N	OCH ₃	carboxyl	hydroxyl
Ethanol	Hymatomelanic	60.94	4.40	0.97	1.75	5.10	2.65
	Humic	61.94	3.31	1.31	—	3.71	2.09
Dioxan	Hymatomelanic	60.26	4.44	1.42	1.38	4.44	2.09
	Humic	61.30	3.44	1.90	—	3.30	1.66

According to Kukhareno, hymatomelanic acids can be formed both by synthesis from the products of decomposition of organic residues and also during the oxidative-hydrolytic destruction of humus substances by oxygen and moisture.



Like humic acids, hymatomelanic acids are heterogeneous; using chromatography, hymatomelanic acids from peats and organic composts were separated by Trojanowski (1952, 1957a, b) into several fractions differing in equivalent weight and fluorescence in ultra-violet light.

Consequently it is considered that hymatomelanic acids are not an independent group of humus substances but an alcohol-soluble fraction of humic acids.

HUMUS SUBSTANCES AS A COMPLEX OF HIGH-MOLECULAR-WEIGHT COMPOUNDS

General ideas on high-molecular-weight compounds¹

At the present time there are no grounds for doubting that humus substances are high-molecular-weight compounds. This idea, which originated in earlier works (Sokolovskii, 1921; Gemmerling, 1921, see 1952; Shmuk, 1924), is being developed at the present time by a number of investigators.

This approach to the study of humus substances, regarding them as high-molecular-weight compounds, is helpful in finding a solution to problems of their genesis, in explaining the reasons for differences in their nature in different soils and in correctly assessing the role of humus substances in soil processes.

During the last few decades, the study of high-molecular-weight compounds has aroused considerable interest in different fields of science and technology. This type of compound (protein, cellulose, lignin, starch, etc.) is widely distributed throughout the animal and plant kingdoms. The common feature of the compounds is the large size of the molecules; this determines some of their properties, and is important because general conceptions and laws of chemistry cannot be applied to phenomena associated with the macromolecule.

High polymers containing molecules of different sizes can be resolved into fractions more uniform in chain length. However, it is impossible in practice to isolate completely homogeneous products from such mixtures. The concept "chemically pure" has, therefore, a specific meaning when used in connexion with high-molecular-weight compounds; by this term a mixture of molecules of different lengths conforming to a similar structural pattern is implied.

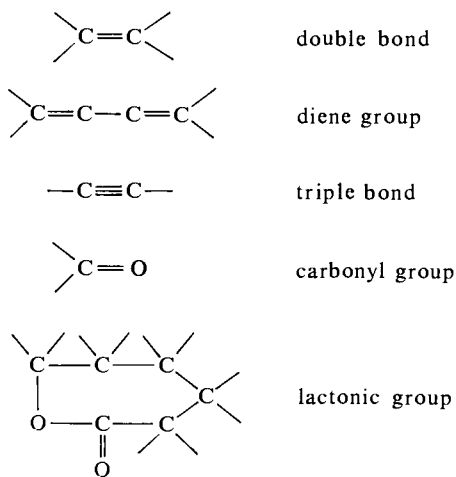
The general structural feature of high-molecular-weight substances is the presence in their molecules of a repeated link. High-molecular-weight compounds are obtained from substances of low molecular weight in two ways: by means of polymerization and by polycondensation reactions.

Polymerization is the process of aggregation of molecules of one or more types, of low molecular weight, into a single molecule of high molecular weight *without the formation of by-products*. This explains the similarity

¹ The account given is from Korshak, V. V. and Rafikov, S. R. (1949, 1950) *The Synthesis and Study of Compounds of High Molecular Weight*, and also from Staudinger (1935).

between the elementary composition of the polymer and that of the original substances.

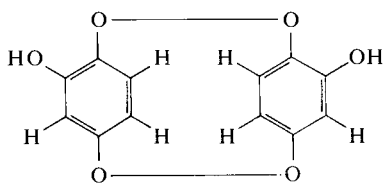
The formation of a polymer from low-molecular-weight compounds takes place when the latter possess groups capable of reacting with other compounds. Such groups are the double and triple bonds, the carbonyl group and sometimes heterocyclic systems capable of fission, e.g.



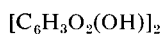
It has been shown that the polymerization process takes place by a chain mechanism involving the action of free radicals which arise at the end of the growing polymer chain. At any moment there are present in the medium the final polymers and the original monomers. The formation of the macromolecule ceases the moment breaking of the chain occurs; this may be the result of a collision with other molecules of the polymer or monomer with the wall of the reaction vessel or with molecules of the solvent.

The cessation of polymerization or its retardation can also occur in the presence of small amounts of such substances as quinone, hydroquinone, etc. These substances (inhibitors) have the capacity of terminating the growing chains by converting the active groups into stable combinations in which the terminal atoms have normal valency. Quinone, for instance, combines readily with the free radical and by this action stops chain growth.

For soil humus we can use as an example the evidence of Eller and Koch (1920) on the possibility of humic-acid formation during the oxidation of phenols according to the following idealized scheme:

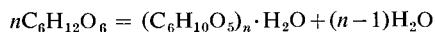


From this scheme it can be seen that the primary molecule of humic acid is a polymer (dimer) of two hydroxyquinones. The formation of the molecules proceeds on the polymerization pattern, as it is not accompanied by the formation of by-products and, therefore, the elementary composition of the polymer is identical with the composition of the original substance (hydroxyquinone):



Without excluding the possibility of the formation of molecules of humus substances by polymerization, it should be recognized that their formation by condensation is more prevalent.

The main distinction between polycondensation and polymerization is in the reaction mechanism. Polycondensation is a reversible exchange reaction occurring during the splitting-off of by-products with the formation of a high-molecular-weight compound. Obviously, in this case, the elementary composition of the condensate differs from that of the original components. The process of polycondensation is brought about by an intermolecular interaction between compounds possessing not less than two functional groups, which are capable of esterification, dehydration, amidation, etc. As distinct from the polymerization reaction, which is of the chain type, the polycondensation reaction has a stepwise mechanism; the growth of the chain results from the interaction of one of the original molecules with another. The obtained product interacts with a third molecule of the original substance, then with a fourth, etc. A condensation reaction involving two or several molecules of the same substance is called homopolycondensation: if molecules of heterogeneous substances participate in this reaction, it is called heteropolycondensation. An example of the former reaction is the formation of dextrin-like products during the treatment of glucose with concentrated hydrochloric acid, which can be represented in the following form (Shorýgin, 1939):



The data presented above indicate that soil humus substances are formed during the condensation of compounds of different nature (for soil humic

acids, these are, hypothetically, aromatic compounds of polyphenol type and products of protein decomposition). Soil humic acids should, therefore, be included in the group of heteropolycondensates.

The nature and properties of the condensation product formed depend to a considerable degree on the ratio of the reacting substances. As an example, we shall present data from the works of Enders (1943), who regards humic acids as products of the condensation of methylglyoxal with amino acids. Enders attempted to reproduce the condensation of these two components experimentally. By varying the ratios of the reacting substances he obtained condensation products with different elementary composition and with different degrees of coloration; this could be judged from the light absorption of the solutions of the condensates. In Table 19 data are presented on the elementary composition and optical properties of condensation products obtained by Enders with different ratios of the original substances. The experiment was carried out by heating for 9 hours on an oil-bath at temperatures of up to 150°.

TABLE 19. CHARACTERISTICS OF CONDENSATION PRODUCTS
(from experiments by Enders, 1943).

Composition of reaction mixture (in solution), in		Elementary composition of heteropolycondensate			Light extinction at 1:100 dilution (%)
methylglyoxal	glycine	C	H	N	
3	30	50.04	6.30	11.39	57
10	23				75
16.5	16.5	60.25	5.00	6.30	70
23	10				50
30	3	62.49	4.79	1.78	30

Enders established that a number of important properties of the condensates formed, such as the degree of dispersion, capacity for dialysis, solubility in water, precipitability with FeCl_3 , HCl , CuSO_4 and CaCl_2 , varied very considerably. Consequently, the nature and properties of humus substances depend not only on the nature but also on the ratio of the substances taking part in the condensation reaction. The fact that the condensation reaction is reversible and in equilibrium is of great importance. Therefore, the isolation of complex high-molecular-weight condensation products is only possible after removal of the low-molecular-weight by-products formed (in particular, water). If the removal of by-products is

unsuccessful, then an equilibrium condition is established and further growth of the chain is prevented.

This condition is undoubtedly of great importance in humus formation in the soil. Excessive soil moisture apparently promotes the formation of humus substances with a smaller size of molecule, because it prevents the removal of condensation by-products (water) and this, in turn, hinders the growth of the molecule. A condition such as this would arise in podzolic and krasnozems soils; in chernozems, on the other hand, which are characterized by a periodic moisture deficit, conditions are favourable for the removal of the water formed as a by-product of the condensation, and this favours the formation of more complex humic acids.

Similar views about the influence of climatic conditions on humus formation were expressed by Bachelier (1960) and Duchaufour (1960). They pointed out that alternate wetting and drying contributes to the condensation and polymerization of humus substances.

Thus, a general consideration of the conditions and mechanism of formation of humus substances leads to the conclusion that the latter represent, in different soils, and even in the same soil, a system of polymers varying in chemical nature and in the size of molecule. With this are connected such important properties as solubility, behaviour towards the coagulating action of electrolytes and certain other properties which govern the participation of humus substances in soil-forming processes.

Humus substances of different soils as a system of polymers

At the present time sufficient data are available to give evidence of differences in the nature of the humic acids of different soils. This problem was referred to earlier during an examination of the elementary composition of humic acids (see Tables 5 and 20).

Differences in the nature of the humic acids were also clearly revealed by the determination of optical properties; this method, first used by Odén (1919), and subsequently by Frömel (1937), Hock (1936, 1937, 1938), Davýdov (1941), Trocmé and Barbier (1947), Aleshin and Zhupakina (1950), Kononova and Bel'chikova (1950) and other investigators, makes it possible to study the aromatic structure of the substance. For humic acids of mineral coal (Kukharensko, 1953) and for soil humic acids (Kononova and Bel'chikova, 1950, 1956; Larina and Kasatochkin, 1957; Kumada, 1955; Orlov, 1959, 1960), a direct relationship between the light absorption of solutions of humates and the degree of condensation of the aromatic ring was reported.

The behaviour of humic acids towards electrolytes (Ca, Fe, Al, etc.) is also characteristic. This is a complex phenomenon which includes the precipitation of salts of humic acids and is complicated by the occurrence of coagulation, depending on the degree of dispersion of the substances. Earlier in this chapter it was mentioned that the degree of dispersion of humic acids is inversely related to the ratio between aromatic (with hydrophobic properties) and aliphatic (with hydrophilic properties) structures in the molecules. Consequently, the greater the predominance of the aromatic ring in the molecules of humic acids the less resistant they are towards electrolytes.

During comparative determinations of the elementary composition, optical properties and behaviour towards electrolytes, a regular pattern of differences in the nature and properties of the humic acids of different soils can be noticed. Springer (1938) showed that humic acids can be classified into two groups according to their optical properties and behaviour towards electrolytes. The first group — brown humic acids (*Braunhuminsäure*) — is characteristic of brown coals, peats and podzolic soils. The representatives of this group are characterized by a lower percentage of carbon, a high degree of dispersion and, therefore, a high resistance to the action of electrolytes.

The second group — gray humic acids (*Grauhuminsäure*) — is characteristic of chernozem soils and rendzinas. This group possesses a high percentage of carbon, a low degree of dispersion and is easily coagulated by electrolytes. This concept of two groups of humic acids differing in elementary composition, optical properties and behaviour towards electrolytes has become firmly established in the literature (Scheffer and Welte, see Welte, 1952; Scheffer, 1954; Duchaufour, 1954). However, under natural conditions the diversity of humic acids is, of course, much greater (Nehring, 1955; Flaig, Scheffer and Klamroth, 1955).

The results of our comparative studies of humic acids and fulvic acids from the major soil types of the USSR showed that there were regular differences in their nature and properties. Differences between the humic acids of different soils can be seen from data on their elementary composition (see Table 20).

The data of Tables 5 and 20 indicate that the percentage of humic-acid carbon increases regularly on passing from podzolic soils to dark-gray forest soil and then to chernozem; a decrease in this value is observed in the soils of dry and desert steppes. An inverse relationship is observed with respect to the percentage of hydrogen. There is a corresponding change in the C:H ratio of the humic acids in the indicated series of soils.

From studies of mineral coals and peats (Kukharenko, 1955) it can be assumed that in soil humic acids the C:H ratio reflects, to some extent, the degree of condensation of the aromatic ring. On this assumption, based on C:H characteristics (see last column of Table 20), it can be concluded that there is an increasing degree of aromatization of the humic acids in a series of soils ranging from podzolic soils to chernozems, and a decrease in the degree of aromatization in chestnut soil and serozem.

TABLE 20. ELEMENTARY COMPOSITION OF HUMIC ACIDS AND FULVIC ACIDS OF THE MAIN SOILS OF THE USSR (AS PERCENTAGES OF ABSOLUTE WEIGHT OF ASH-FREE MATERIAL)*

Soils		C	H	O	N	C:H
Northern podzol under forest; humus illuvial horizon 16–24 cm; Arkhangel region	I	58.11	5.37	32.00	4.52	10.82
	II	52.37	3.53	42.89	1.21	14.84
Sod-podzolic soil, arable; 0–20 cm; Moscow region	I	57.63	5.23	32.33	4.81	11.02
	II	42.63	5.05	44.60	4.12	9.15
Dark-gray forest soil under oak; 12–19 cm; Shipov forest, Voronezh region	I	61.20	3.60	31.32	3.88	17.00
	II	47.46	3.64	45.87	3.03	13.04
Ordinary chernozem, arable; 0–20 cm; Kamennaya Steppe, Voronezh region	I	62.13	2.91	31.38	3.58	21.35
	II	44.84	3.45	49.36	2.35	13.00
Chestnut soil, virgin land; 0–20 cm; Valuisk Exp. Sta., Stalingrad region	I	61.74	3.72	30.62	3.92	16.60
	II	43.19	3.61	51.43	1.77	11.96
Light serozem, arable; 0–20 cm; Pakhta-Aral, Kazakhsk SSR	I	61.94	3.93	29.46	4.67	15.76
	II	45.80	4.30	46.00	3.90	10.65
Krasnozem under fern; 0–20 cm; Anaseuli, Georgian SSR	I	59.65	4.37	31.54	4.44	13.65
	II	49.82	3.35	44.33	2.50	14.87

* I represents humic acids

II represents fulvic acids

This conclusion is in agreement with the data from X-ray analysis (see the section "The structure of the humic-acid molecule", p. 73). The aromatic structure is more distinct in humic acids from chernozems and less clear in humic acids from podzolic soil.

No regular differences are observed in the elementary composition of fulvic acids of different soils. The somewhat higher percentage of carbon

found in fulvic acids of podzolic soils, krasnozems and gray forest soil can be attributed to contamination with humic acids, which in these soils are partially soluble in acids. Owing to the weak expression of the aromatic structure the C:H ratio in fulvic acids is not characteristic.

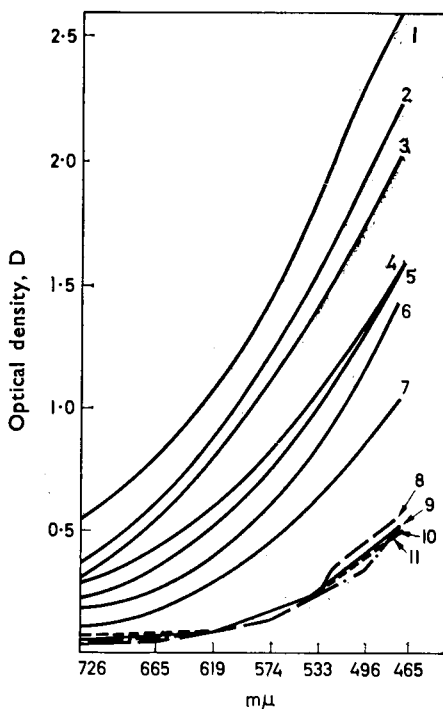


FIG. 10. Optical density (D) of humus substances.

Humic acids: 1. Ordinary chernozem; 2. Dark-gray forest soil; 3. Chestnut soil; 4. Light serozem; 5. Sod-podzolic soil; 6. Krasnozems; 7. Strongly podzolic soil. *Fulvic acids*: 8. Krasnozems; 9. Light serozem; 10. Strongly podzolic soil; 11. Ordinary chernozem.

The data of Fig. 10 show that the light absorption of solutions of humates from different soils increases in the order: strongly podzolic soil—krasnozem—sod-podzolic soil—serozem—chestnut soil—dark-gray forest soil—ordinary chernozem.

Fulvic acids have an extremely low optical density and are placed near humic acids from strongly podzolic soil. From a consideration of the earlier statement—that the light absorption of humic acids depends directly on the degree of condensation of their aromatic ring (and from the data on elementary composition)—it can be concluded that the degree of con-

densation of the aromatic ring of humic acids increases on passing from podzolic soils to chernozems.

These conclusions are in conformity with values characterizing the behaviour of humus substances towards electrolytes (CaCl_2). As can be seen from Table 21, humic acids from chernozem are the least stable towards CaCl_2 , rapidly coagulating even with small amounts of the electrolyte.

TABLE 21. THRESHOLDS OF PRECIPITATION (COAGULATION) OF HUMUS SUBSTANCES (IN MILLIEQUIVALENTS CaCl_2 CALCULATED PER LITRE OF SOLUTION CONTAINING 0.136 g CARBON OF HUMIC AND FULVIC ACIDS)

	Strongly podzolic soil	Sod-podzolic soil	Krasnozem	Dark-gray forest soil	Ordinary chernozem	Dark chestnut soil	Light serozem
Humic acids	40	20	18	16	5	8	14
Fulvic acids	precipitation (coagulation), slight						

Fulvic acids are the most stable, followed closely by humic acids from strongly podzolic soil, the latter being incompletely precipitated even with the addition of large amounts of CaCl_2 . All the remaining soils occupy an intermediate position between these two extremes.

It has already been stated that the degree of dispersion of humic acids, determining their behaviour towards electrolytes, is inversely related to the ratio between aromatic and aliphatic structures in the molecule. Hence, the lowering of the threshold of coagulation with an increase in the degree of aromatization of the humic acids (from podzolic soils to chernozems) is a regular phenomenon.

The behaviour of humic acids with respect to coagulation by electrolytes – characterizing the degree of dispersion – is undoubtedly of great importance in soil processes such as the translocation of humus substances and their organo-mineral compounds in the soil profile, the formation of soil structure and also the intensity of the action of humic acids on the mineral constituents of the soil. The most highly dispersed, and therefore the most mobile are the humic acids from strongly podzolic soil, which have at the same time the least favourable properties with regard to the formation of soil structure. Humic acids from chernozems are less mobile and participate actively in soil aggregation.

The examples given indicate that humic acids of different soils cannot be regarded as equal in value (from the point of view of their nature and properties). In some soils (for instance, in strongly podzolic soil) they are closer in their nature and functions to the fulvic acid group than to humic acids from chernozem soil. We shall discuss this in greater detail giving a number of concrete examples for different soils in Chapter 6.

Humus substances of a single soil as a system of polymers

The statements made here on the nature of humus substances and the mechanism of their formation provide a complete basis for assuming that in any soil, humus substances represent a heterogeneous mixture of molecules. Interesting results were obtained by Flaig and Beutelspacher (see Flaig, 1958) from ultracentrifuge determinations of the weight of humate-particles. It was found that the particles were not completely mono-dispersed; their weight varied within the range of 30,000–50,000. A small fraction of the humate precipitated rapidly; apparently, this fraction consisted of particles of greater weight than those of the first group. Moreover, a weak pale-yellow solution containing particles with a weight of less than 10,000 remained above the precipitate after many hours of centrifugation.

Recently a number of authors have demonstrated that humus substances are heterogeneous; using various methods such as fractional precipitation by acids and buffer solutions, electrophoresis and chromatography, they have shown that humus substances may be separated into a number of fractions and that humic acids and fulvic acids are related. The methods used are described in Chapter 8, "Methods of investigating soil organic matter" in the section "Methods of fractionating humus substances", where the literature is quoted. Here discussion is limited to a few examples.

After isolating humic and fulvic acids from a deep chernozem, Aleksandrova (1949) obtained by fractional dialysis a number of fractions which differed in elementary composition, exchange capacity and behaviour towards electrolytes. A gradual change in the nature of the fulvic and humic acid fractions indicates the "closing" of these two groups (Table 22).

Kaurichev, Fedorov and Shnabel' (1960) obtained interesting results during the fractionation by electrophoresis of humic and fulvic acids isolated from various soils. They determined the optical density of the separated fractions, and found that the fractions with high optical density predominated in humic acids from soils of the chernozem type, while fractions with low optical density and fluorescence characteristic of fulvic

TABLE 22. ELEMENTARY COMPOSITION, EXCHANGE CAPACITY AND BEHAVIOUR TOWARDS ELECTROLYTES OF FULVIC AND HUMIC ACID FRACTIONS FROM A DEEP CHERNOZEM
(Aleksandrova, 1949)

Substance	Fraction	Elementary composition, % of ash-free substance				Exchange capacity meq per 100 g at pH 6.0-6.5	Precipitation by cations*
		C	H	O	N		
Fulvic acids	Diffusing through cellophane	44.00	5.90	42.50	7.6	Not determined	Fe^{3+}
	Not diffusing through cellophane	50.44	5.20	39.50	4.86	Not determined	$\text{Fe}^{3+}, \text{Ba}^{2+}$
Humic acids	From sol of: Fraction 1	52.85	4.92	37.29	4.91	320	$\text{Fe}^{3+}, \text{Ba}^{2+}, \text{Ca}^{2+}$
	Fraction 2	54.15	4.72	37.11	4.02	458	$\text{Fe}^{3+}, \text{Ba}^{2+}, \text{Ca}^{2+}$
	Fraction 3	60.33	4.53	31.45	3.69	537	$\text{Fe}^{3+}, \text{Ba}^{2+}, \text{Ca}^{2+}, \text{H}^{+}$

* ——— complete coagulation; — partial coagulation; little coagulation.

acids predominated in humic acids isolated from podzolic soils and krasnozems.

We reached similar conclusions from fractionating humus substances by partition paper chromatography. The chromatograms of fulvic and humic acids from a chernozem and from podzolic soils showed three zones

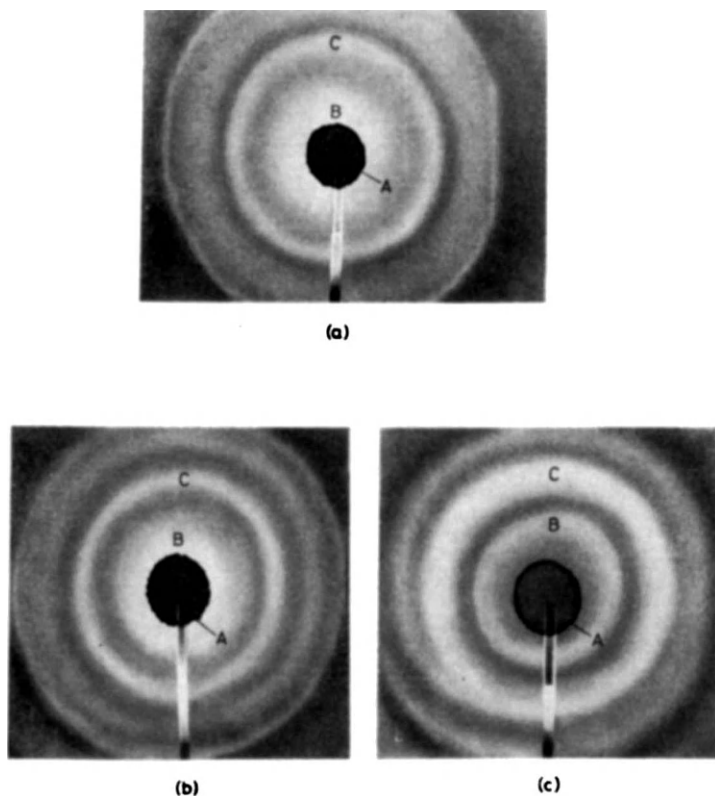


FIG. 11. Chromatograms of humus substances in ultra-violet light. a: Humic acids from ordinary chernozem. b: Humic acids from sod-podzolic soil. c: Fulvic acid from sod-podzolic soil. A — centre zone; B — intermediate; C — peripheral (fluorescent).

in ultra-violet light: a central zone A where the substance was initially deposited; an intermediate zone B; and a peripheral fluorescent zone C (Fig. 11).

We investigated the nature of the substances extracted from the zones and found that the fraction in zone C resembled fulvic acids in a number of characteristics (C and H contents, optical density); these ("fulvic acid-

like") fractions are present in large amounts in humic acids from a podzolic soil and in smaller amounts in humic acids from a chernozem (Kononova and Bel'chikova, 1960).

Fractionation of humus substances by paper electrophoresis has confirmed these results (Kononova and Titova, 1961). Under ultra-violet light, three zones appeared on the electrophoretograms of humic acids (from a chernozem, a sod-podzolic soil and the humus-illuvial horizon of a strongly podzolic soil) and of fulvic acids: a zone A where the substance was initially deposited; a zone B, negatively charged and moving towards the anode; and a zone C which was most mobile and fluorescent.

In addition the distribution of the substances between the zones varied with the sample taken; the negatively charged fraction B predominated in humic acids from the humus-illuvial horizon of the strongly podzolic soil and in fulvic acids, whereas this fraction was much smaller in humic acids from the chernozem. Humic acids from the sod-podzolic soil were intermediate. This is illustrated in Fig. 12, which shows the electrophoretograms and densitometer traces obtained.

The experiments described above show that humic acids and fulvic acids are heterogeneous and consist of fractions generally similar to each other. Differences in the nature and properties of the various representatives linked by intermediate forms are, to a considerable extent, determined by the ratios of the fractions.

An interesting and important inference can be made from these experiments: it is possible that humic and fulvic acids represent not independent groups of humus substances but a single sequence linked by a chain of inter-conversions. Similar deductions could also be made from the work of Scheffer and Welte (1950a, b), Laatsch (1944, 1948, 1950), Schlichting (1953), Welte (1952), and Hayashi and Nagai (1962).

It is well known that after the dialysis of humic-acid gel a certain part is capable of passing through a semi-permeable membrane (cellophane, parchment). This fraction is represented, apparently, by simpler forms of humic acid, which are soluble in water. Yet, according to generally accepted ideas, solubility in water is considered to be a property characteristic of fulvic acids, but not of humic acids.

Moreover, there are observations indicating that fulvic acids can acquire the property characteristic of humic acids—the capacity for precipitation in an acid medium; the formation of a brown flocculent precipitate during concentration of a solution of fulvic acids is of normal occurrence. Laatsch (1944, 1948) observed the formation of a brown flocculent precipitate characteristic of humic acids after prolonged dialysis of a solution

of fulvic acids (from strongly podzolic soil) followed by evaporation to 1/10 volume in a vacuum at a temperature not exceeding 35° C.

With subsequent dilution of the concentrated fulvic-acid solution to the original volume with 1 per cent NaF the precipitate dissolved, and

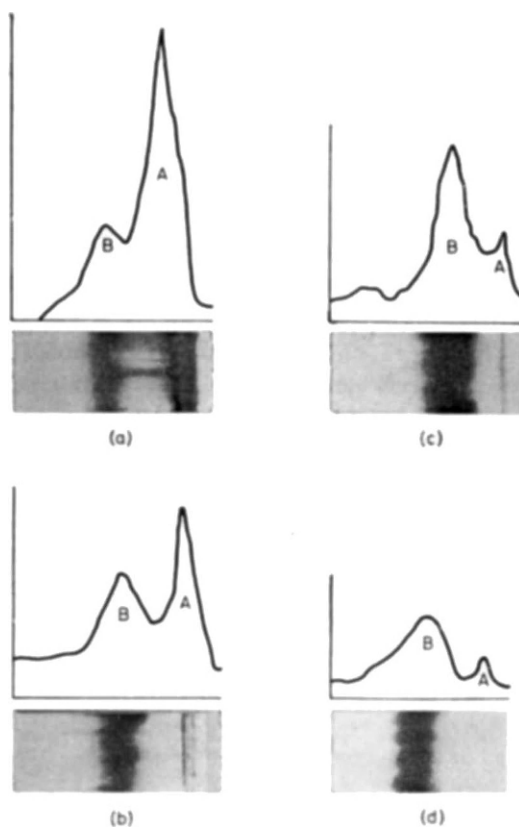


FIG. 12. Electrophoretograms and recording densitometer curves of humus substances. Humic acids: a. chernozem; b. sod-podzolic soil; c. humus-illuvial horizon. Fulvic acids: d. krasnozem. Zones: A. start; B. mobile, negatively charged.

with the addition of HCl reprecipitation occurred. Thus, a part of the original fulvic acids acquired the property characteristic of humic acids — the capacity for coagulation in an acid medium.

The existence of intermediate forms between the humic-acid and fulvic-acid groups was shown by Schlichting's investigations (1953). Schlichting found that a fraction of the humic acid isolated from peat-podzolic soil and rendzina by treatment with sodium pyrophosphate precipitated

at pH 2.5. These are "true humic acids". The second fraction remains in the solution and only precipitates after further acidification with HCl to a concentration of 2 per cent. This fraction possesses features typical of humic acids—solubility in acid solutions—and is represented apparently by intermediate forms between humic acids and fulvic acids; Schliching called them "humo-fulvic acids".

Freytag (1955, 1961), Misterski and Łoginow (1959), Nikolaeva (1958, 1959) and Aleksandrova and Andreeva (1963) discuss the physico-chemical nature of the conversion of humic acids into fulvic acids and the reverse process which occurs as the result of changes in the colloidal state. From the data given it can be seen that the division of humus substances into humic acids and fulvic acids as individual groups has lost its importance. At the present time, the majority of investigators favour the view that fulvic acids are the initial forms or the decomposition products of humic acids.

It should be mentioned that under natural conditions the development of the podzol-forming process favours the formation of humus substances primarily of fulvic-acid type (i.e. initial forms of humic acids). The reverse condition is found in chernozems, where humus substances are represented primarily by humic acids, which are, moreover, of complex nature (with a condensed aromatic ring). This view has arisen from data given in the present chapter and also from data on the composition of humus (on the relationship between the conditions of soil formation and the nature of the humus, see Chapter 6).

CONCLUSIONS

From this review of present ideas on the composition of soil humus and the nature of humus substances it is clear that this study has been fraught with considerable difficulties; nevertheless, a number of controversial and obscure aspects are now becoming fairly clear.

Thus, it has been confirmed that the whole diversity of soil organic substances can be classified into two groups:

1. Compounds of a non-specific nature related to various classes of organic chemistry (here are included the decomposition products of the original plant and animal residues and elements of the plasma of micro-organisms).
2. Strictly humus substances which are specific high-molecular-weight compounds of a complex nature.

The isolation of humus substances from the soil from decomposing plant residues by means of mild treatments and in the form of aqueous solutions leaves no doubt that humus substances exist as natural products.

With the conception of humus substances as a system of high-molecular-weight compounds, it is also plain that the approach of investigators of the last century from the standpoint of classical chemistry—regarding them as chemically individual compounds—was incorrect. The attempts of investigators to isolate separate representatives of humus substances in a chemically pure form and to identify them according to their molecular weight, elementary composition and certain other properties (e.g. solubility) regarded as constant features, led to the discovery of numerous and diverse substances, each one being regarded as an independent representative and given a special name. This introduced confusion into ideas on the composition of humus substances and into their classification.

The data accumulated from a study of the nature and structure of humus substances indicate the actual presence in the soil of only two groups: humic acids and fulvic acids. From the investigations described in the present chapter it may be presumed that fulvic acids are the lowest or simplest representatives of humic acids. So acidification of alkaline extracts should perhaps be regarded not as a means of separating fundamentally differentiated groups—fulvic acids and humic acids—but rather as one of the ways of fractionating humic acids.

With regard to the other groups of humus substances, *humins* of the soil medium do not appear to be a separate group of humus substances but are apparently humic acids occurring in a stable link with the mineral part of the soil; the humins group is in part represented by plant and animal residues which have become carbonized. Nor is there a sound foundation for the separation of *hymatomelanic acids* as an independent group, for they represent the alcohol-soluble fraction of humic acids and perhaps, partially, resin acids.

Being related to the group of high-molecular-weight compounds humic and fulvic acids are group conceptions uniting substances which, although they possess a common structural pattern, are not completely identical.

On the basis of general theoretical views on the condensation reaction, which is the basis of the synthesis of humic acids and of fulvic acids, differences between the separate representatives of these groups can be explained by: (1) the different composition of the original compounds (aromatic substances, protein decomposition products, reducing substances) taking part in the heteropolycondensation reaction; (2) the varying ratio

of the reacting substances; (3) the conditions of the medium, in particular, the possibility of the removal of by-products of the condensation.

Regular differences between the humic acids can be seen—in a series of soils ranging from podzolic soils to chernozems humic acids appear to increase in complexity. Thus, humic acids of different soils should not be regarded as equal in their effect on soil-forming processes. In strongly podzolic soils and in krasnozems, humic acids, in their functions, more closely resemble fulvic acids than humic acids from sod-podzolic soils and especially those from chernozems. A further detailed study of the nature and properties of humus substances in various soils should be the present-day trend in soil-humus investigations.

At the same time, the need for a further study and classification of the highly diverse group of organic compounds of non-specific nature present in the soil should not be overlooked. In spite of the fact that they occur in quite small amounts, these substances undoubtedly have an important influence on soil phenomena.

The study of the chemical nature and properties of humus substances should not be carried out without an elucidation of their origin and the mechanism of their formation. Only by combined studies will it be possible to form a correct assessment of the genetic relationship or principal differences existing between the different representatives of humus substances which will provide a basis for their rational classification.

CHAPTER 3

THE BIOCHEMISTRY OF HUMUS FORMATION

THE ROLE OF PHYSICAL, CHEMICAL AND BIOLOGICAL FACTORS

THE CHIEF sources of humus substances in the soil are the organic residues of plant and animal origin. Under the conditions in Central Europe, the amounts entering the soil may be estimated from the following approximate values: under annual and perennial grass vegetation, and also in forest soils with a grass cover, the weight of roots dying annually equals 3–5 tons/hectare; a similar amount enters the soil in the form of leaf-fall. The mass of micro-organisms dying during one year amounts to 1 ton/hectare, and the bodies of dead animals to several hundred kg/hectare (Tyurin, 1946).

Humification of organic residues entering the soil depends upon their chemical composition and upon conditions in the soil influencing the activity of the micro-organisms.

Although the plant organisms generally contain the same groups of substances (waxes, fats, resins, proteins, simple and complex carbohydrates, lignins, and other components) the proportions of these substances in different plants are extremely variable, and this materially affects the humification rate. The chemical compositions of higher and lower plant organisms are given in Table 23.

On reaching the soil, organic residues of plant and animal origin undergo diverse changes brought about by various factors. Some of these changes can undoubtedly take place without the participation of micro-organisms and animals; they can be classed as follows:

1. Destructive changes due to the physical action of natural factors (the effect of atmospheric precipitation, wind) and to the action of man (soil cultivation).
2. Changes in the chemical nature of organic residues under the direct action of water, light, air and reaction of the medium, e.g. the oxidation of fats and resins in light, the oxidation of aromatic compounds at alkaline

TABLE 23. APPROXIMATE CHEMICAL COMPOSITION OF HIGHER AND LOWER PLANT ORGANISMS (as % of dry matter)

Organisms investigated	Waxes, fats, resins	Protein	Cellulose	Hemicelluloses and soluble carbohydrates	Lignin
Perennial leguminous plants					
Roots	10—12	10—15	20—25	25—30	10—15
Leaves	—	12—20	15	10—12	5
Perennial grasses					
Roots	5—12	5—10	25—30	25—30	15—20
Deciduous species					
Leaves	3—5	4—10	15—25	10—20	10
Wood	—	0.5—1	40—50	20—30	20—25
Coniferous species					
Needles	20—25	5—7	20	15—20	15
Wood	—	0.1—1	45—50	15—25	25—30
Mosses	—	5—10	15—25	30—60	None(?)
Lichens	—	3—5	5—10	60—80	8—10
Algae	—	10—15	5—10	50—60	None
Bacteria	—	40—70	None	Slime	None

soil pH, the hydrolysis of certain compounds in the presence of excessive moisture at acid or alkaline soil pH.

3. Changes resulting from the effect of tissue enzymes, whose action, in dead cells, has a uni-directional, predominantly oxidative character. Such changes include the oxidation of tannin-like substances, soluble polyphenols and aromatic amino-acids with the formation of complex, dark-coloured condensation products; the formation of dark pigments during the withering of the tea leaf is a typical example of these reactions. The important role of oxidizing enzymes of decomposing tissues in humus formation was pointed out by Trusov (1916b), Maiwald (1931), Tyurin (1937), Mishustin (1938) and other authors.

In noting the importance of these factors in the transformation of organic residues, we should bear in mind the fact that neither of them individually, nor all of them in combination, can bring about humification in the absence of the activity of micro-organisms and animals.

The humification process of plant and animal residues as a whole can be explained only by considering the activity of the various representatives of the microflora possessing differentiated fermentation mechanisms and

the work of microscopic and macroscopic animals in processing organic residues.

In explaining the role of micro-organisms in this process I will again mention that humus formation is a complex two-stage process in which organic residues of plant and animal origin undergo profound transformations involving:

1. The decomposition of the original components of tissues and their conversion by micro-organisms into simpler chemical compounds and partially to products of complete mineralization (CO_2 , NO_2 , NO_3 , NH_3 , CH_4 , H_2O , etc.).

2. The synthesis of organic compounds with the formation of high-molecular-weight humus substances of specific nature. For example, the humic-acid molecule (see Chapter 2) is formed during the condensation of aromatic compounds with amino acids or peptides, with the possible participation of reducing substances.

According to generally accepted views, micro-organisms participate mainly in the first stage of humus formation—the decomposition of the original organic residues—and the synthetic activity of micro-organisms is limited to the resynthesis of bacterial plasma. With regard to the condensation reactions which take place in the second stage of humus formation, they are considered to be physico-chemical, occurring without the participation of micro-organisms.

However, the results of many investigations lead us to suppose that this second stage also takes place with considerable participation of micro-organisms. Trusov (1916, 1917), from his own numerous investigations and from the work of Abderhalden, Semuel, Bürkel and Bertrand (see Chapter 1), concluded that humus substances originate from compounds such as tannin-like substances, aromatic amino acids and lignin, which have a tendency to form quinones. Their conversion into humus substances proceeds as follows: (1) the oxidation of the aromatic compounds by tissue oxidases and micro-organisms with the formation of quinones; (2) subsequent condensation of the quinones with their conversion into humus substances. Thus, according to Trusov's views, developed later by Maiwald (1931), the oxidizing enzymes of plant tissues and micro-organisms, as *biocatalysts*, are an important factor in the completion of the second stage of humus formation—the synthesis of the molecules of humus substances. Trusov's ideas on the role of oxidizing enzymes of micro-organisms in humus formation have been confirmed experimentally at the present day; this matter will be discussed later.

THE ORIGIN OF HUMUS SUBSTANCES

The question of the origin of humus substances attracted a great deal of attention even as early as the middle of the last century—the initial period of soil-humus studies. However, owing to the fact that at that time soil microbiology was in its infancy, humus formation was regarded as a chemical process and not as a biochemical one. In accordance with these views, the oxidation of organic compounds (proteins, carbohydrates, encrusting substances, etc.) by heating or boiling with acids and alkalis was the common method of reproducing the humification of plant materials experimentally; examples of this can be found in the experiments of Berzelius, Mulder, Sestini, Malaguti, Chevreul and Liebig. The dark-coloured substances, soluble in alkali and precipitated by acids, which were obtained by this treatment were considered to be identical with the humic acids isolated from soils, decomposing plant residues and peats of various origin.

However, a comparison of the elementary composition of natural humus substances with that of artificial preparations showed that there were essential differences between them. While the artificial humus-like substances (except those obtained from proteins) were free from nitrogen, all natural humus substances contained as a rule 3–4 per cent nitrogen. This fact indicated the occurrence of more complex paths in the humification of plant residues and the possible participation of several components of plant tissues in the formation of humus substances. This aspect, however, did not receive due attention from the investigators at that time, who regarded nitrogen not as a constituent of humus substances but as a contaminant which they tried to eliminate by means of careful purification.

In spite of obvious dissimilarities with natural conditions, the chemical method of reproducing humification mentioned above was used not only during the early stages but also at later periods of soil-humus investigation. Mention should be made here of the works of Willstätter and Zechmeister (1913) who oxidized cellulose in an autoclave under conditions of high temperature and pressure and obtained light-coloured products. This work was later used by followers of the lignin theory of the origin of humic acids as evidence against the role of cellulose in humus formation.

Later, Fischer and Schrader (1921–1922) subjected lignin to alkaline oxidation in an autoclave; the dark-coloured oxidation products obtained were regarded by them as evidence of a lignin origin of humic acids. The related works of Eller and Koch (1920), of Orlov and Tishchenko (1931) and of several others come into this category.

In examining the problem of the origin of humus substances, the results of experiments carried out under conditions of great artificiality and dissimilarity from natural conditions can only be used with great caution.

With the development of soil microbiology and the elucidation of the role of micro-organisms in the natural cycle of substances, investigators began to study the problem of the origin of humus substances under conditions which would allow biological activity to proceed. A fault of these experiments was that they were carried out with isolated plant substances or at the best with artificial mixtures. Such were the works of Hoppe-Seyler (1889), Snyder (1898), Suzuki (1906–1908) and also Trusov's early works. These investigators were not sufficiently aware of the fact that their experimental conditions were also artificial, as the synthesis of humus substances is the result of a complex reaction between several compounds. Therefore, the study of this process with whole plant residues, in which the possible sources of humus substances occur in natural combinations, is the nearest approach to natural conditions. Such a course of investigation was chosen by Kostychev (1886, 1889).

In a series of experiments with various plant residues (litter of woody species, grass vegetation)—observing the change in appearance and anatomical structure of the residues, studying the change in their chemical composition, explaining the role of micro-organisms and insects in this process—Kostychev by such multilateral investigations brought to light very important points which were later confirmed and developed by many investigators: the transformation of the nitrogen of plant residues into bacterial plasma, the non-lignin origin of humus substances in the early stages of humification of plant residues, etc. In later studies of the origin of humus substances, many investigators, in reproducing the process of humus formation, used whole plant residues. There are, for instance, the well-known works of Kravkov (1906, 1908, 1911), who concluded from his experiments on the decomposition of plant residues that water-soluble organic compounds of plant tissues undoubtedly participate in humus formation. The fact that tannin-like substances are sources of humus substances during the early stage of humification was later made more precise by Kravkov's pupil Trusov (1916).

A study of the origin of humus substances using whole plant residues was carried out extensively during the 1920's and '30's during the course of investigations on the chemistry of peat, brown coal and coal.

We can include in this category the works of Wehmer (1915, 1925, 1927), Rose and Lisse (1917), Bray and Andrews (1924), Grüss (1928), Grosskopf (1926, 1928, 1929, 1935), Falck (1927, 1928, 1930), Kürschner

(1927), Fischer and Lieske (1928), Brandl (1928), Waksman (1936), and other authors. Their results served as one of the pillars of the lignin theory of the origin of humus substances. As a result of these works it was thought that the carbohydrate fraction of plant residues, in particular cellulose, was not of essential importance in the formation of humus substances due to its rapid decomposition by micro-organisms to end-products of mineralization (CO_2 and H_2O) and to a certain amount of acid of low molecular weight belonging to the fatty series. Lignin (a component of plant residues more resistant to decomposition), which is subjected during humification to complex physico-chemical changes, is eventually converted into humic acids.

However, owing to the narrowness of the approach to the study of this process (mainly limited to a comparative determination of the group composition of plant residues) a number of very important aspects of this process—the sequence in decomposition of the tissues, the development of bacteria in them and the character of the participation of decomposition products of plant residues and of bacterial plasma in the new formation of humus substances—escaped the attention of investigators.

It was, in fact, investigations on the change in the anatomical structure of the conifer needle during humification that enabled Grosskopf (1929, 1935) to establish the extremely important fact of the formation of dark-coloured humus-like substances at the site of the decomposition of the cellulose walls of parenchyma cells. The formation of humus substances during cellulose decomposition was also observed by Waksman and Heu-kelekian (1926).

Imperfections in the works of the last century and the data of recent years on the nature of lignin and cellulose and on the possible courses of their conversion during the decomposition of plant residues prompt us to turn to an examination of the question of the participation of these components in the formation of humus substances, which was so hotly debated in the 1920's and '30's and which was apparently settled satisfactorily in favour of lignin.

THE POSSIBLE PARTICIPATION OF LIGNIN IN THE FORMATION OF HUMUS SUBSTANCES

There were no doubts in the minds of most investigators about the importance of lignin as a source of humus substances. Even in the last century some chemists (Mulder, Liebig and others) regarded encrusting substances as the main source of humus. Observations on the humification

of wood under natural conditions, and also the relative ease with which humus-like compounds were obtained during the treatment of lignin with alkali solutions, were regarded as evidence for the definite participation of lignin in the formation of humus substances.

Hoppe-Seyler (1889), who was unable to obtain humus substances during the decomposition of isolated cellulose and hemicelluloses, although in similar experiments with wood the latter turned brown rapidly, also supported the theory of the participation of lignin in humus formation. Slezkin (1900), indicating the similarity in composition between the ash of humus and that of encrusting substances, was not in any doubt as to the participation of the latter in humus formation. Hébert (1892) and Dehérain (1902) pointed out in their works that humus is a mixture of lignin and proteins.

Detailed investigations on the problem of the possible participation of encrusting substances in humus formation were carried out by Trusov (1916). In his experiments, birch and Scots-pine sawdusts were decomposed either alone or mixed with proteins or plant residues (maple leaves). In addition, in some cases the sawdust received a preliminary treatment with boiling water, ethyl ether or diastase to free the lignin from contamination with other plant substances—readily soluble carbohydrates, fats and proteins. It was found that sawdust by itself humified fairly slowly and that the process was accelerated by the presence of protein substances.

Trusov demonstrated that lignin oxidation was accelerated in a medium made alkaline by the presence of ammonia produced by the decomposition of protein by fungi. This was in agreement with investigations of the last century (T. Hartig and R. Hartig) in which it was noted that during the decomposition of wood by certain fungi (*Trametes*, *Agaricus*, *Polyporus*) a considerable amount of humus substances passed into solution on treatment of the humified wood with cold ammonia.

We have already indicated the works of the 1920's and '30's on lignin decomposition which were connected with investigations on the chemistry of the humus substances of peat and coal.

These works demonstrated the resistance of lignin to decomposition compared with other components of plant tissues and this was considered to be evidence in support of the lignin theory of the origin of humic acids. There were a number of indications, too, that lignin had an inhibiting effect on the decomposition of other plant substances, e.g. cellulose, when it acted as a barrier to the action of bacteria on them (Boruff and Buswell, 1934).

The belief that lignin was relatively resistant to the action of micro-organisms was in agreement with the ideas of that period on its chemical nature. According to Fuchs's hypothesis, which was accepted at that time, the basis of lignin is a condensed, extremely resistant, cyclic grouping (pyrene ring) (see Fig. 13).

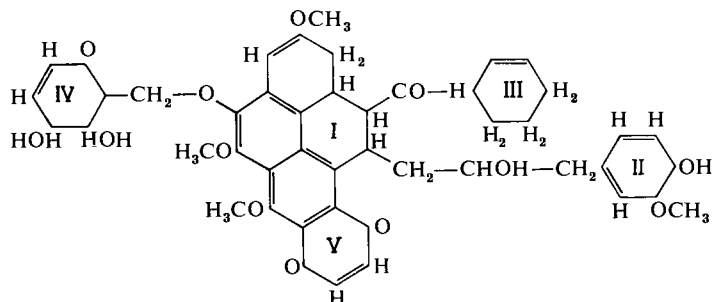
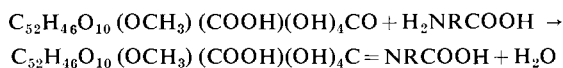


FIG. 13. Structure of the lignin molecule (according to Fuchs).

In accordance with ideas on the chemical stability of lignin and its low availability to micro-organisms, the conversion of lignin into humic acids was regarded not as a biochemical process but as a physico-chemical one. It was assumed that the changes which occur during this process consist of a loss of some functional groups (methoxyl OCH₃) and the gain of new ones (carboxyl COOH); it was thought, however, that no profound destructive changes occurred in lignin during this process.

This conception is reflected in Waksman's well-known hypothetical equation, according to which the lignin molecule reacts with the protein molecule to form a "ligno-protein complex":

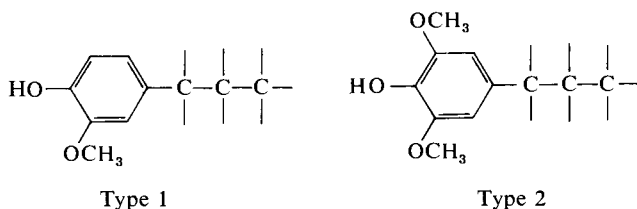


Investigations carried out in recent years have introduced new ideas on the nature of lignin, the mechanism of its formation and its decomposition. In the light of this, Fuchs's hypothesis that lignin is a unique, highly-resistant substance is found to be inadequate. Moreover, new investigations on the utilization of aromatic compounds by micro-organisms as a source of energy makes it necessary to reconsider the question of the participation of lignin in humus formation. We shall now continue with a review of the more important works in this field.

An obstacle which considerably handicapped studies on the nature of lignin was the use of drastic methods (strong acid and alkali solutions) which inevitably produced changes in the lignin molecule.

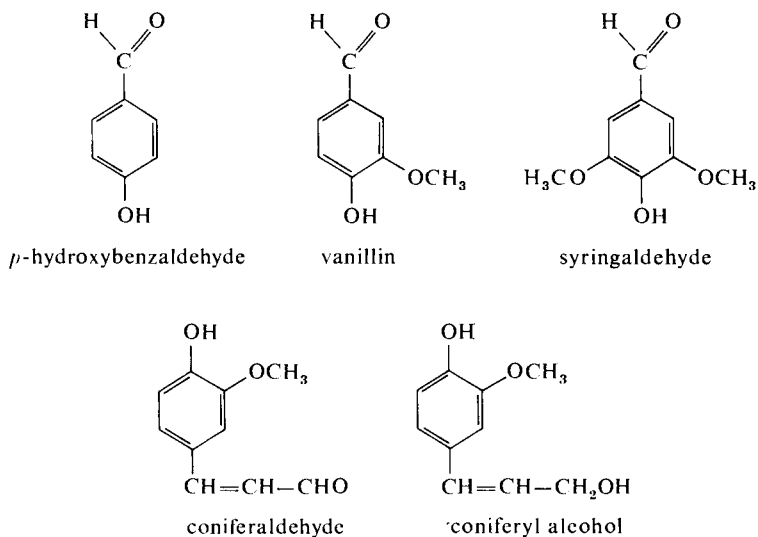
Of interest in this connexion are the milder methods of lignin isolation¹, in particular by means of alkaline nitrobenzene oxidation (Freudenberg and co-workers, 1936, 1938, 1940; Hibbert, 1941, 1942), by treatment with metallic sodium in liquid ammonia (Shorygina and Kefeli, 1947), by extraction of the plant material with ethanol (Brauns, 1952) or by the isolation of "enzymatically liberated" lignin from wood decomposed by fungi (Chudakov, 1949; Odintsov and Shishkova, 1952; Stevens and Nord, 1954). Lignin closest to its natural form is isolated from plant material by the method of Björkman (1956, 1957); the material is ground in a vibratory ball mill and subsequently extracted with dioxan.

Using these methods, Type 1 compounds of the phenylpropionic series were isolated from the lignin of coniferous species and Type 2 compounds from the lignin of deciduous species:



By means of oxidation with nitrobenzene in an alkaline medium at 160° under pressure, vanillin, syringaldehyde, coniferaldehyde, *p*-hydroxybenzaldehyde and other related compounds were isolated from the wood of various coniferous and deciduous species.

¹ For literature on this subject, see: Nikitin, N. I. (1948) New investigations on the chemistry of wood and cellulose, *Trudy Inst. Lesa Akad. Nauk SSSR* Vol. 2; Manskaya, S. M. (1947) The formation of lignin in plants, *Uspekhi sovremennoi Biologii* Vol. 23, No. 2; (1957) The biosynthesis and decomposition of lignin, *Uspekhi sovremennoi Biologii* Vol. 44, No. 1(4); Odintsov, P. N. (1949) Advances in the chemistry of lignin, *Trud. Inst. lesokhozyaistvennykh Problem, Akad. Nauk latv. SSR*, No. 1; Shorygina, N. N., Kefeli, T. Ya. and Semendina, A. F. (1948) Contribution to the problem of the structure of lignin, *Gidroliznaya Promyshlennost' SSSR*, No. 2; Brauns, F. (1948) *Lignin, Fortschritteder Chemie organischer Naturstoffe*, Vienna: Springer; Bardinskaya, M. V. (1953) Lignin and its formation in the plant, *Uspekhi sovremennoi Biologii* Vol. 35, No. 2; Nikitin, N. I. (1951) *The Chemistry of Wood*, Moscow: Izd. Akad. Nauk SSSR; Shorygina, N. N. and Izumrudova, T. V. (1959) Present ideas on the structure, properties and utilization of lignins, *Khimicheskaya Nauka i Promyshlennost'* Vol. 4, No. 6; Brauns, F. (1952) *The Chemistry of Lignin*, N. Y.; Brauns, F. and Brauns, D. (1960) *The Chemistry of Lignin*, suppl. volume, N.Y. and London; Brown, S. (1961) The chemistry of lignification, *Science* Vol. 134, 3475.



The results of these works are in agreement with Klason's views, according to which the basis of the lignin molecule is an aromatic ring similar in structure to coniferyl alcohol (Klason, 1922, 1931, 1932).

According to Freudenberg's hypothesis, which is the most comprehensive of those examined, the lignin molecule is built up by the continuous etherification of phenylpropane derivatives. Then follows the process of cyclization of the side chains with a neighbouring aromatic ring. As a result of etherification and cyclization, a chain-like molecule consisting of 7–10 units of phenylpropane is formed (Fig. 14).

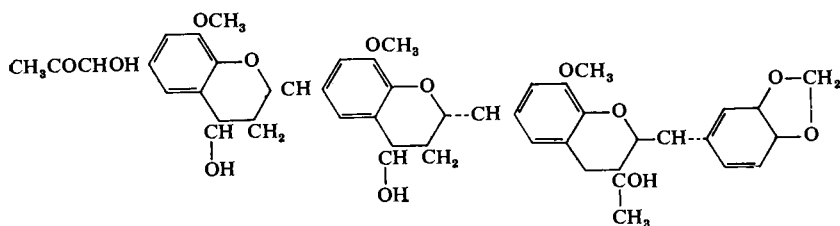


FIG. 14. The structure of the lignin molecule (according to Freudenberg).
 A recent scheme given by Brauns for the structure of lignin is shown in Fig. 15.

However, it appears that in the lignin molecule simpler linkages are also present, e.g. by a single oxygen bridge only; the linkage between separate units in the molecule may have the character of a simple ether.

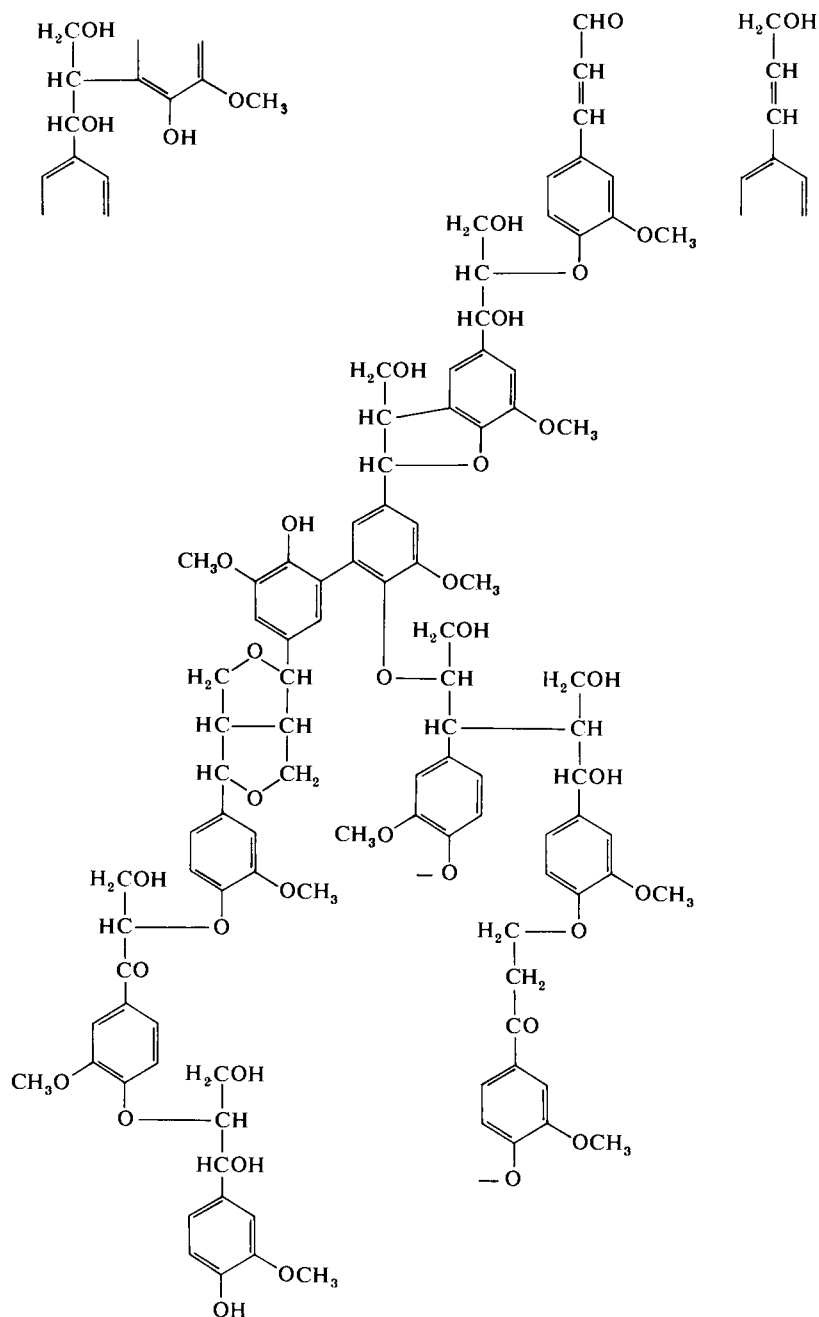


FIG. 15. The structure of lignin (according to Brauns).

The presence in lignin of simple phenols possessing a 3-carbon-atom chain is of great importance for understanding the process of lignin formation. As is well known, phenols of similar structure are capable of taking part in oxidation, condensation and self-condensation reactions, and therefore they are the true precursors of lignin.

A number of new suggestions on the mechanism of lignin formation have also been put forward. Until recently, the formation of lignin in the plant was regarded as a physical impregnation of the maturing cell with an inert substance (lignin). Contemporary biochemical studies, however, indicate that this process occurs only in the living condition and is closely linked with the respiration of the cell.

Wood cells are formed from the living cambial tissue and the division, enlargement and thickening of the cell wall accompanied by lignification occur only in living cells. According to Hibbert, the substances of the phenylpropane series which are considered to be the precursors of lignin also function as respiratory catalysts in the plant cell. These substances are capable of oxidation-reduction reactions because of the presence

in them of the ene-diol grouping $\text{HO}-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}=\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-\text{OH}$ and represent an oxidation-reduction system resembling the quinone-hydroquinone system.

Hibbert thus believes that in both higher and lower plants mono-molecular propylphenols (lignin precursors) are synthesized and function as respiratory chromogens, being apparently hydrogen carriers.

The subsequent fate of these phenols differs in different plants: in the lower plants (e.g. mosses, lichens and algae) they remain in simple forms; in the higher plants, respiratory catalysts, which function at first in simple forms, are oxidized in a post-mortal environment and rapidly undergo oxidation by condensation and polymerization reactions, being converted into more complex forms. Hibbert's conception of mono-molecular propylphenols as respiratory catalysts is actually a development of Palladin's striking observations on the importance of simple phenols of the pyrocatechol series as hydrogen acceptors in the respiratory process (among them, Palladin included coniferyl alcohol, vanillin, dihydroxyphenylalanine or aminohydrocaffeic acid). Palladin referred to glycosides as the "pro-chromogens" of respiration. Oparin (1921-1927) isolated chlorogenic acid (a depside of quinic and caffeic acids) which corresponds to the respiratory chromogen.

The works so far mentioned are concerned primarily with the study of lignins of woody species. Unfortunately, investigations on the lignin of grass vegetation have not been numerous (Hibbert, 1942; Bondi and

Meyer, 1948). They suggest that lignin formation proceeds here in much the same way as in woody species, although it has a certain specificity. Bondi and Meyer studied the lignin of grasses and legumes (*Eragrostis tef*, *Setaria italica*, *Hordeum murinum*, *Trifolium alexandrinum*, *Arachis hypogea* and some other species) to determine its digestibility to animals. They isolated lignin by means of dilute alkali (0.5 N NaOH) then freed it from carbohydrate contaminants. Using alkaline-nitrobenzene oxidation they isolated vanillin and *p*-hydroxybenzaldehyde. During fusion with concentrated KOH, all lignins produced catechols and protocatechuic acids. By the ethanolysis of lignins (alcohol + 3 per cent H₂SO₄ at 170–180°) derivatives of the phenylpropane series were detected.

	N (%)	OCH ₃ (%)
Lignin of hard woody species	none	20.0
„ „ soft woody species	0.2–0.3	15.0
„ „ grasses	1.2–1.6	10.0
„ „ legumes	2.9–3.4	5.0

Bondi and Meyer concluded on the basis of obtained data that the lignin molecule of grass vegetation consists of three aromatic rings of molecular weight 600. Unlike the lignin of woody species, lignins of grasses all contain nitrogen and are characterized by a lower methoxyl content, which is in inverse relationship with nitrogen.

So far it is not clear whether the nitrogen in lignin is an admixture difficult to separate (see Odintsov and Sergeeva, 1949), or whether it is a constituent part of the molecule; this is certainly of interest and requires further investigation.

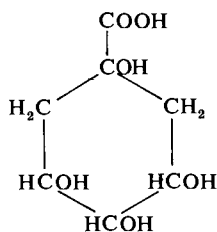
The extremely important point that lignin synthesis in the plant involves the participation of oxidizing enzymes was established during recent years. Manskaya (1947, 1948), Freudenberg and Richtzenhain (1943), Manskaya and Emel'yanova (1940, 1942), in a number of model experiments with pyrocatechin, tannin from tea leaves, alcohol extract from oak shavings and aromatic derivatives of lignin, showed convincingly that in the presence of peroxidases (from horse radish) the oxidation of the original substances is activated with the formation of dark-coloured condensation products. Similar results were obtained by Freudenberg and Richtzenhain during the oxidation of substances of the guaiacic and syringic series by an enzyme obtained from the juice of mushrooms.

The enzymatic oxidation of phenols is of widespread occurrence in the plant kingdom under natural conditions particularly during the formation of tannic substances from lignin, during lignification, cutinization and other processes (Oparin, 1935; Kursanov and co-workers, 1943, 1947; Bokuchava, 1948, 1950; Prokoshev, 1943; Mikhlin, 1947; and others).

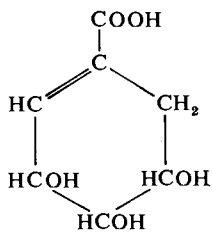
Manskaya (1948, 1952), during a study of the oxidizing processes occurring in wood in connexion with lignin formation, showed that cambial tissues and wood of the new annual ring in Scots pine contain β -glucosidase and the oxidizing enzymes, peroxidase and polyphenol oxidase; the coniferin of cambial tissues and its derivatives serve as a substrate for oxidizing enzymes. In the living cells of the cambial tissue the oxidation-reduction processes are in equilibrium and as a result of this the oxidation products of phenols do not accumulate in the cells. When the cells die off during lignification, oxidizing processes predominate over reducing processes. The products obtained as a result of enzymatic oxidation are converted by subsequent condensation into lignin and deposited in the cell walls of the xylem.

The views that have been mentioned on the participation of a system of oxidizing enzymes in the lignification process have been confirmed by many investigators during recent years (Freudenberg, Reznik and co-workers, 1952; Freudenberg, 1955; Higuchi, Kawamura and Ishikawa, 1953; Mason, 1955; and others).

Of particular interest is the way in which the structural units of lignin are formed. Recently, a number of authors have paid particular attention to shikimic acid as a precursor of the aromatic structural units of lignin; this acid is similar to quinic acid and, like the latter, is found in plants (Paeck, 1950; Brown and Neish, 1955; Manskaya and Kodina, 1958, 1960; Zaprometov and Silina, 1960).



quinic acid



shikimic acid

Quinic acid is genetically related to glucose and in the metabolism of substances in the plant may be an intermediate link between carbohydrates

and aromatic compounds (Kizel', 1928; Kursanov and co-workers, 1950, 1952).

In recent works dealing with lignin formation, fundamental changes have been introduced into previous theories on the nature and origin of lignin and the mechanism of its formation.

Obviously, the earlier conceptions in which lignin of various plant materials was regarded as some unique stable substance are no longer tenable. According to Fuchs, a very stable pyrene ring is present in the lignin molecule. The great diversity of lignins, the presence in their molecule of substances of aromatic nature capable of various reactions of self-condensation, oxidation and condensation, the association between lignification and the respiratory process and the genetic relationship between lignins and simple phenols of the phenylpropane series, which act as respiratory catalysts, all introduce new conceptions into the theory on the possible role of lignin in humus formation.

Evidently, in plant tissues, particularly in grass vegetation, lignins of different groups occur:

1. Precursors of lignin (monomolecular phenylpropanes and their early stages of oxidation and condensation).
2. Lignin formed in the lignified tissues (xylem vessels, endodermis, etc.).

Lignins of the first group are rapidly involved in humus formation during the early stages of humification of the plant residues. With regard to the second group of lignins, their participation in humus formation apparently takes place at later stages after the preliminary decomposition of the lignified tissue.

The investigations of Philips, Weihe and Smith (1930), Norman and Jenkins (1934), Norman (1936), Khan (1940) and other authors have shown that lignin of plant tissues can be utilized by micro-organisms. Fungi—*Fusarium*, *Trichoderma*, *Agaricus campestris*, *Coniophora*, *Polyporus*, *Poria*, etc.—play an active role in this process (Waksman, 1931; Waksman and Hutchings, 1936; Falck, 1927–1930; Wehmer, 1925, 1927; Chastukhin, 1945, 1948, 1953; Pelczar, Gottlieb and Day, 1950; Rypáček, 1960; Haider *et al.*, 1962, etc.). The ability to break down lignin is possessed by a number of bacteria, in particular those belonging to the species *Pseudomonas* and *Flavobacteria* (Sørensen, 1962).

The work of a number of authors (Gottlieb *et al.*, 1951; Broadbent, 1954; Henderson, 1955, 1957; Flaig, 1958b; Flaig, Schobinger and Deuel, 1959a; Flaig and Haider, 1961; Ishikawa, Schubert and Nord, 1962) shows that the role of lignin in humic acid formation can be represented as

follows. During humification of plant residues by the action of micro-organisms, lignin is freed from its combination with other plant substances, in particular, cellulose.

In a review, Fischer (1953) has pointed out that, during the decomposition of lignified tissues by natural processes, the glucosidic link between lignin and carbohydrates is first broken. Changes in lignin begin with the loss of methoxyl and methyl groups; new carboxyl groups appear in the lignin, their number increasing as humification progresses (Odintsov and Kreitsberg, 1954; Flaig, 1958b; Flaig, Schobinger and Deuel, 1959a).

It is very important to note that the products of lignin decomposition may interact with other compounds, in particular the products of micro-organism metabolism. The experiments of Flaig *et al.* (1959a) are relevant here. Wheat straw was allowed to decompose at optimum temperature and moisture, NaNO_3 being added as a source of nitrogen. With progressive decomposition of the straw, the percentage of carbon in the lignin decreased, and the percentage of nitrogen increased (Table 24). At the same time, part of the nitrogen consisted of α -amino acids, which were apparently metabolic products of the micro-organisms decomposing the straw.

TABLE 24. CHANGE IN THE NATURE OF LIGNIN DURING HUMIFICATION
(Flaig, Schobinder and Deuel, 1959a)

Duration of experiment, days	Elementary composition, %				OCH_3 %	Acid groups, m eq per 100 g substance
	C	H	O	H		
0	58.59	5.60	31.37	0.54	15.33	178
70	58.79	5.93	29.48	2.01	11.14	173
180	58.67	5.91	29.15	2.37	9.06	233
260	58.00	5.83	29.93	3.14	7.84	
340	54.97	5.96	32.09	3.08	8.54	243
410	54.29	5.86	32.88	2.97	7.32	

However, "structural units" of lignin do not always take part in the formation of humus substances. In nature, micro-organisms capable of assimilating aromatic compounds as a source of energy are of widespread occurrence. Thus, Störmer (1908) and Sen Gupta (1921) indicated the disappearance of certain antiseptics, e.g. toluene, xylol, cresol and phenol from soils, and attributed this to the decomposition of these substances by the soil microflora.

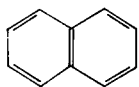
Wagner (1914) isolated and studied various bacteria utilizing phenols and their derivatives—phenol, pyrocatechol and phloroglucinol—as a

source of energy. Waterman (1915) found that *Penicillium glaucum* utilizes phenol, pyrocatechol, hydroquinone, phloroglucinol, protocatechuic acid, gallic acid, hydroxybenzoic acid and quinic acid as sources of energy. Butkevich (1925) showed that the mould fungi *Aspergillus niger* and *Citromyces glaber* can assimilate a number of polyphenols: pyrocatechol, resorcinol, hydroquinone and pyrogallol.

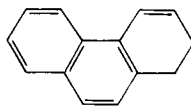
Finally, the works of Gray and Thornton (1928) and Tattersfield (1928) should be mentioned. They isolated from the soil of Rothamsted Experimental Station a number of bacteria belonging to the families: Coccaceae, Mycobacteriaceae, Bacteriaceae, Bacillaceae, Spirillaceae, etc., which were capable of decomposing phenols, *o*-, *m*- and *p*-cresol, naphthalene, phloroglucinol, resorcinol and toluene.

Recent investigations have shown that micro-organisms (fungi, bacteria and yeasts) utilize phenolic-type compounds and their derivatives (Bernheim, 1940, 1941, 1942; Happold, 1930, 1950; Newman and Thomas, 1949; Gall, 1952; Knösel, 1958; Henderson, 1961; etc.). In addition, certain bacteria are able to decompose not only simple but also condensed compounds with two or three aromatic nuclei characteristic of crude oil and coal.

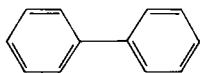
Thus, Tauson (1927) isolated three species of *Bact. naphhtolinicus* utilizing naphthalene as a source of energy. Later (1928), he isolated three species of *Bact. phenanthrenicus*, which oxidized phenanthrene (an aromatic hydrocarbon with three condensed rings) and also a number of cyclic compounds, mainly benzene derivatives. He reported that the bacteria that he had isolated were capable of oxidizing a number of polynuclear aromatic hydrocarbons: diphenyl, dibenzene, stilbene and anthracene (1929, 1932).



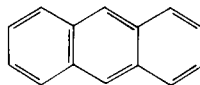
naphthalene



phenanthrene

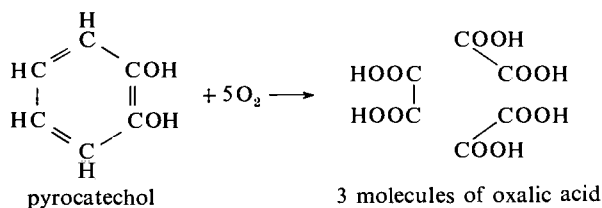


diphenyl



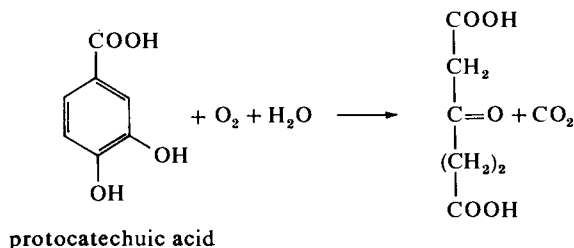
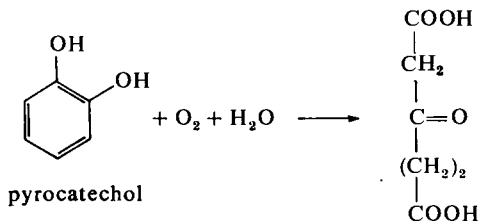
anthracene

With regard to the decomposition mechanism of aromatic compounds, Tauson assumes that it takes place with the formation of an oxygenated



Evans (1947) investigated the oxidation of phenols by the micro-organism *Vibrio* 01 by estimating the amount of carbon dioxide evolved in a Warburg apparatus and by determining the intermediate products formed by the metabolism of the micro-organism. He found that in the oxidation process phenols and benzoic acid are converted into intermediate aromatic compounds in which, subsequently, a fission of the ring occurs with the formation of low-molecular-weight organic acids (muconic, oxalic, etc.) and also end-products of mineralization.

Aromatic compounds in the polyphenol group are decomposed by micro-organisms (*Vibrio* 01, *Pseudomonas*) according to the mechanism revealed by the work of Evans, Smith and Linstead (1951), Kilby (1951), Fernley and Evans (1958), Coulson and Evans (1959), Ribbon and Evans (1962), Sleeper (1951) and Stanier, Sleeper *et al.* (1948, 1950, 1954). The latter found that the oxidation of aromatic compounds with simplification of the molecule takes place by ring fission with the formation of aliphatic keto-acids:



Konetzka *et al.* (1952) and Tabak *et al.* (1959), who studied the decomposition of α -conidendrin (which is related to the lignins) by the bacteria *Pseudomonas* and *Flavobacteria*, give an analogous pathway for the pro-

cess. They point out that the transformation of the substance proceeds *via* demethoxylation, formation of vanillic acid and then protocatechuic acid. Subsequent oxidation of this latter compound breaks the aromatic ring and β -keto-adipinic acid is formed.

The same conclusions follow from the work of Haider, Soun-uk-Lim and Flaig (1962), who studied the transformation of ^{14}C -labelled lignin and its constituent structural units.

Thus, it can be seen from an examination of works on the decomposition of aromatic compounds by micro-organisms, that various groups of the latter are capable of utilizing aromatic compounds as a source of energy by bringing about ring fission with the subsequent production of low-molecular-weight organic acids and end-products of mineralization.

As a result of these works it became clear that previous views on lignin as a substance resistant to microbial action are without foundation. While this biological action is taking place the lignin undergoes decomposition with the formation of simple aromatic compounds which either take part in a condensation reaction with other substances to form a primary molecule of humus substance or are involved in further microbiological processes and may be decomposed by ring fission into compounds of the aliphatic series (low-molecular-weight organic acids); in this case the role of lignin in the formation of humus substances is excluded.

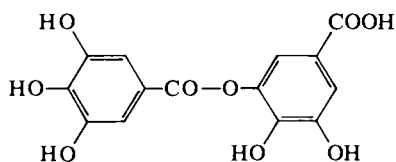
Similar views on the participation of lignin in the formation of humic acids were expressed by Kurbatov (1953), Rakovskii (1953), Flaig (1955) and Ploetz (1954). In accordance with these views we cannot accept the ideas of Mattson and Koutler-Andersson (1942, 1943) and those of certain other investigators (see Bremner's review paper, 1954) who are of the opinion that lignin is converted into humic acids as a result of autoxidation and the appropriation of nitrogen.

The essential change in lignin during humification of plant residues explains the observation by a number of authors (Jenkinson, 1956; Jenkinson and Tinsley, 1960; Tinsley and Zin, 1954; and Swaby—see the reference in the work of Davies, Coulson and Lewis, 1960), that lignin as such cannot be extracted from the soil, in spite of its regular addition in plant residues.

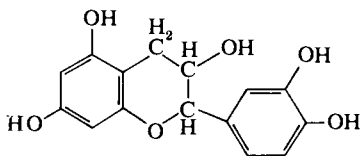
THE POSSIBLE PARTICIPATION OF TANNINS IN THE FORMATION OF HUMUS SUBSTANCES

The participation of tannins in humus formation has certain features in common with the process described above for lignin. The various tannins may be classified into two groups. The first group consists of tannins

which are hydrolysed by acids or enzymes (e.g. tannase) and decomposed into compounds with lower molecular weight; it includes lecanoric acid, gallic acid and ellagic acid. These substances are easily hydrolysed because they contain ester and glucosidic bonds. The second group consists of condensed tannins, such as complex derivatives of catechins.



m - Digallic acid

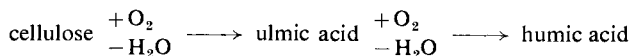


Catechin, *dl* - Epicatechin

The participation of tannins, both simple and condensed, in the formation of humus substances begins with the liberation of polyphenols which are subsequently oxidized and these products then condense further with amino acids and proteins. At the same time, the oxidation of the polyphenol components of tannins can be terminated, as with lignins, by fission of the aromatic ring and formation of aliphatic substances which are subsequently mineralized.

THE POSSIBLE PARTICIPATION OF CELLULOSE AND OTHER CARBOHYDRATES IN THE FORMATION OF HUMUS SUBSTANCES

On this question highly controversial opinions can be found. Suffice it to say here that in the middle of the last century cellulose was regarded as a direct source of humus substances and the process of its conversion was believed to be an oxidation and dehydration without preliminary hydrolytic decomposition. Thus, according to Mulder this process was as follows:



With the development of the biological trend in soil humus studies another point of view appeared which regarded cellulose as an indirect source of humus substances being converted first into microbial plasma. This view was expressed in its clearest form by Trusov.

Finally, there was also a third point of view, based on the works of Hoppe-Seyler (1889) and Omelyanskiĭ (1899, 1902) on the decomposition

of cellulose by anaerobic bacteria. These investigations showed that cellulose is fermented completely with the formation of end-products of mineralization and certain quantities of low-molecular-weight organic acids. As a result of this work the importance of cellulose in the formation of humus substances was almost completely excluded. This evidence was used by followers of the lignin theory of humic-acid origin as proof of the correctness of their views.

In spite of the existence of a large number of works devoted to cellulose decomposition, little is known about the biochemistry of the decomposition with different groups of micro-organisms (fungi, bacteria and actinomycetes). In most cases investigators confined themselves merely to a statement of the fact of decomposition and the most they did was to indicate the amount of cellulose decomposed during the experimental period.

In the last few decades a number of works have appeared on the aerobic decomposition of cellulose by myxobacteria. Bacteria of this group have a wide distribution in various soils and are particularly numerous in cultivated soils, forest litter, rotting plant residues, peats, muddy deposits and even in sea water (Vinogradskii, 1929; Isachenko and Vakengut, 1932; Rubenchik, 1932; Stapp and Bortels, 1934; Rokitskaya, 1933; Krzemieniewska, 1933; Imshenetskiĭ and Solntseva, 1936, 1937; Mishustin, 1938; Stanier, 1942; Harmsen, 1946; and others). Owing to the fact that the majority of myxobacteria utilize various carbohydrates besides cellulose as a source of energy, their role in the transformation of the carbohydrate components of plant residues is undoubtedly very great.

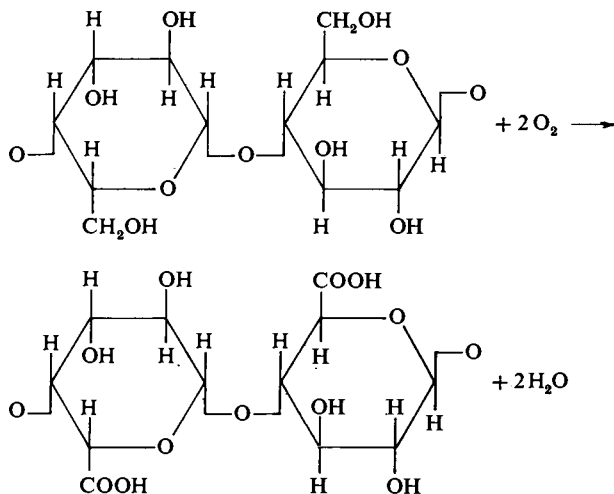
The study of this group of bacteria was first begun by Van Iterson (1904) and Kellerman and McBeth (1912). The uniqueness of their developmental cycle and their systematic position have now been established. In the opinion of some investigators (Jahn, 1924; Imshenetskiĭ and Solntseva, 1945; Stanier, 1947; Harmsen, 1946) myxobacteria can be classified into a number of groups on the basis of certain characteristics of their morphology and life-cycle.

The first investigations on the biochemistry of cellulose decomposition were carried out by Hutchinson and Clayton (1919). *Spirochaeta Cytophaga*, which they isolated, decomposed cellulose very vigorously, two-thirds of the total amount being mineralized completely and the remainder being converted into various fermentation products, mainly low-molecular-weight organic acids (butyric and acetic acids) which cannot serve as sources for the formation of humus substances. In this process, Hutchinson and Clayton recorded the formation of peculiar slimy substances which resembled pectins and pectic acids. These substances were precipitated by

Ca, Mg and Al salts and also by lead acetate. They were soluble in alkali solution and were precipitated by acids in the form of gels. Hutchinson and Clayton therefore concluded that these substances are isolated from the soil as constituents of humic acids.

Some other authors have stated in their works that various cellulose myxobacteria produce this unique group of slimy substances but their origin has been explained in different ways. According to Vinogradskii (1929) cellulose decomposition by myxobacteria has the character of an oxidation in which cellulose, *without preliminary hydrolytic decomposition*, is converted into a pectin-like substance of oxy-cellulose type; part of the latter is water-soluble and is precipitated in the form of a gel upon the addition of acids. Vinogradskii detected nitrogen in the composition of these slimy substances and he regarded the plasma of myxobacteria as its source.

Loitsyanskaya (1937), who shared Vinogradskii's views, is of the opinion that cellulose is oxidized by myxobacteria, the oxidation starting with an alcohol group CH_2OH and resulting in the formation of a product of oxy-cellulose (or uronic-acid) type. Loitsyanskaya, in fact, succeeded in demonstrating the evolution of CO_2 and the formation of furfural when the products of cellulose decomposition were boiled with 12 per cent HCl. The scheme of cellulose oxidation by myxobacteria was represented as follows:



Walker and Warren (1938) reached similar conclusions. They regarded the uronic acids which they detected during cellulose decomposition as cellulose oxidation products.

This point of view, however, was certainly not shared by all investigators. Imshenetskiĭ (1938), Norman and Bartholomew (1940), Fuller and Norman (1943) and Stanier (1942) believe with good justification that the oxidation of cellulose to oxy-cellulose cannot explain the "energetics" of the process because cellulose can only be utilized by myxobacteria as a source of energetic material after preliminary hydrolysis to soluble dialysable substances capable of diffusing through bacterial cell-walls.

According to these authors, the action of myxobacteria on cellulose begins with its hydrolysis and proceeds with the fermentation of products of the hydrolysis to CO_2 and H_2O . Imshenetskiĭ did, in fact, detect glucose among the products of cellulose decomposition, which confirmed the data previously obtained by Pringsheim (1909). In the opinion of Imshenetskiĭ and others (Norman, Stanier) the slimy, humus-like substances soluble in alkali and precipitated by acids represent not oxy-celluloses but products of resynthesis — bacterial slime and bacterial pigments.

A comparison of the view of the authors mentioned above shows that during the last two decades two points of view have again arisen with regard to the possible participation of cellulose in the formation of humus substances. In accepting Vinogradskiĭ's view (also that of Loitsyanskaya, Walker and Warren) that the oxidation of cellulose with the formation of oxy-cellulose is the first stage of the process, cellulose should be regarded as a direct source of humus substances. However, on the basis of Imshenetskiĭ, Norman and Stanier's views on the hydrolytic decomposition of cellulose at the first stage of the process, cellulose should be regarded as an indirect source of humus substances through products of bacterial resynthesis.

To find out which point of view was correct we carried out experiments on the decomposition of cellulose by myxobacteria isolated from humifying plant residues¹. The cultures of myxobacteria isolated showed some differences with respect to the size of the cells, the form of the reproductive bodies and the behaviour towards different carbohydrates. One of the isolated cultures, distinguished by its strong activity, was found to be similar to that isolated and described by Imshenetskiĭ and Solntseva (1937) — *Sorangium cellulosum*. The fact that these cultures utilized glucose, galactose, arabinose, xylose, lactose, maltose, dextrin and starch, besides cellulose, left little doubt that myxobacteria take part in the decomposition of hemi-

¹ The detailed layout of the experiments and the results are given in Kononova, M. M. and Aleksandrova, I. V. (1949) The participation of cellulose myxobacteria in the process of humification of plant residues, *Mikrobiologiya* Vol. 13, No. 1.

celluloses, pectic substances and other carbohydrate components of plant residues in addition to cellulose.

These micro-organisms utilize all the inorganic forms of nitrogen (NH_3 , NO_2 , NO_3) as nitrogen sources. Of the organic forms asparagine was assimilated; the other nitrogen-containing organic compounds investigated, i.e. aspartic acid, peptone, legumin and globulin, were only assimilated very weakly.

We also carried out experiments using liquid cultures of Hutchinson's medium. For better aeration, filter paper cut into strips was placed on the glass drain at the bottom of the flask. At the end of the experimental period (usually 20 days) the paper remaining was washed with water, dried and weighed.

The washings together with the medium, were filtered first through linen and then through filter paper; the organic carbon in the liquid was then determined and the balance of organic substances calculated. The results of the experiment were as follows:

	Expt. 1	Expt. 2
Amount of cellulose applied	2.00 g	1.00 g
Amount remaining at end of expt.	1.54 g	0.80 g
Amount of cellulose decomposed	0.46 g	0.20 g
As % of original amount of cellulose	23	20
Amount of carbon of decomposed cellulose	0.184 g	0.08 g
Total amount of carbon found in medium	0.051 g	0.016 g
As % of total amount of carbon of decomposed cellulose	28	20

The data given indicate that of the total amount of cellulose decomposed approximately 3/4 was mineralized completely to CO_2 and H_2O , and only 1/4 remained in the medium in the form of organic substances; evidently the latter are products of myxobacterial activity.

Similar results were obtained in Expt. 3 in which glucose was used instead of cellulose. By determining the amount of glucose and the total carbon remaining in the medium, it was found that during 20 days, 86 per cent of the total amount of applied glucose had been decomposed, 2/3 of this being completely mineralized and only 27 per cent occurring in the form of organic compounds produced by myxobacterial activity.

	Expt. 3
Amount of glucose applied	0.800 g
Amount remaining at end of expt.	0.113 g
Amount of glucose decomposed	0.687 g
As % of original amount of glucose	86
Amount of carbon of glucose	0.275 g
Total amount of carbon found in medium	0.092 g
As % of total amount of carbon of decomposed glucose	33

We then tried to elucidate the nature of the organic substances formed during cellulose decomposition and to establish the presence of uronic acids among the decomposition products. For this purpose the combined medium from several flasks was evaporated under neutral conditions under reduced pressure and carefully centrifuged to remove the bodies of the myxobacteria; volatile acids, uronic acids, furfural, reducing substances and protein nitrogen were determined in the liquid (Table 25).

TABLE 25. THE COMPOSITION OF PRODUCTS OF THE DECOMPOSITION OF CELLULOSE AND GLUCOSE BY MYXOBACTERIA, MILLIGRAMS IN THE LIQUID

Expt.	Organic carbon in liquid	Organic carbon of volatile acids	Uronic acids	Furfural	Protein nitrogen	Reducing substances after hydrolysis with 2% HCl
With cellulose	204	32	traces	traces	4.32	none
With glucose	368*	40	traces	traces	5.12	none

* After deduction of the remaining unfermented glucose.

Table 25 shows that the products of cellulose decomposition include a certain amount of volatile acids and soluble proteins produced by myxobacterial resynthesis but only a negligible amount of uronic acids and furfural; reducing substances are absent.

The composition of the relatively large amount of organic compounds present in the medium remains obscure. However, a most interesting point became clear; when at the end of the experiment the bodies of the myxobacteria (slime) were removed, neither uronic acids nor furfural were detected in the medium.

The results suggest that the decomposition of cellulose by myxobacteria has the character, not of an oxidation, but of an extensive hydrolysis, the products of which are utilized as a source of energy by the bacteria. The oxy-celluloses (uronic acids) are, apparently, not products of cellulose oxidation, but products of resynthesis by myxobacteria (slime). An analysis of the plasma of cellulose myxobacteria did, in fact, show the presence of 4–12 per cent uronic acids.

In this connexion we share the views expressed by Imshenetskiĭ and other investigators (Norman, Stanier). However, even simple comparison of the elementary composition of the plasma of cellulose myxobacteria with that of humic acids of plant residues shows that there are essential differences between them (Table 26). These differences are apparent from a determination of the exchange capacity, indicating that the acidic groups (COOH) are absent from the plasma of cellulose myxobacteria.

TABLE 26. ELEMENTARY COMPOSITION OF MYXOBACTERIAL PLASMA AND OF HUMIC ACIDS AS PERCENTAGE OF ABSOLUTE DRY ASHLESS MATERIAL

Investigated materials	%C	%H	%O	%N	C:N	Exchange capacity (m eq per 100 g substance)
Myxobacterial plasma	52.85	7.86	26.59	12.7	4.1	18.9
Myxobacterial plasma	51.30	8.00	28.70	12.0	4.2	—
Humic acids from plant residues	57.40	5.65	32.35	4.95	11.5	167.9

Therefore, even if the participation of cellulose in the formation of humus substances during its decomposition by myxobacteria is brought about through the products of bacterial resynthesis, there are still no grounds for identifying the latter with humus substances.

In the light of recent works the participation of cellulose as well as other carbohydrates in the formation of humus substances is held to be the result of extensive transformations closely associated with metabolic processes occurring in the cells of micro-organisms (mould fungi, actinomycetes, bacteria).

There is now substantial evidence about this problem from work with cultures of fungi, bacteria and actinomycetes; metabolic products aromatic in nature have been found in nutrient media containing carbohydrates. Amongst early investigations, the work of Muschel (1922), Lemoigne (1928) and Prevot and Saissac (1947) should be mentioned. Raistrick and

co-workers (Raistrick, Anslow, Simonart, Oxford *et al*, 1931–1951) whose work was begun before the war, have investigated the problem for many years. Fungi — *Aspergillus*, *Penicillium* — were grown in Czapek's synthetic medium containing sugar, and derivatives of phenolcarboxylic acids (benzoic and salicylic acids, etc.) were isolated from the culture solution and identified. These compounds of an aromatic nature that are products of micro-organism metabolism undoubtedly may serve as structural units in a molecule of humus substance.

Similar views on the part played by products of micro-organism metabolism in the formation of humus substances are expressed in the work of many investigators (Laatsch, 1948, 1950, 1952; Scheffer, Plotho and Welte, 1950; Springer and Wagner, 1952; Welte, 1952; Plotho, 1950, 1951; Tepper, 1952, 1960; Flaig, 1952; Flaig and Küster, 1952; Küster, 1952a, 1954; Mishustin, Dragunov and Pushkinskaya, 1956; Shivrina, 1962).

We have observed the formation of dark-coloured humus-like substances in synthetic media containing sugar as the sole source of carbon when these were infected with the fungi *Aspergillus niger* and *Penicillium* (Kononova and Aleksandrova, 1956, 1958). Similar phenomena were observed by Aleksandrova (1962) in experiments with *Actinomyces globisporus roseus*. In all the experiments proteins and also amino acids and aromatic compounds (pyrocatechol and protocatechuic acid) were detected in the culture solution (see Fig. 16).

Humus-like substances were isolated from the culture solution in the following way. The liquid was carefully filtered, dialysed and electro-dialysed; it was concentrated in a vacuum at 35° C and air-dried in thin layers in dishes. The chemical analyses of humus substances isolated from the culture solution of micro-organisms are given in Table 27. All these substances are acid in nature with exchange capacities of 200–300 m eq per

TABLE 27. CHEMICAL PROPERTIES OF HUMUS SUBSTANCES ISOLATED FROM MICRO-ORGANISM CULTURE SOLUTIONS

Micro-organisms	Elementary composition %						Exchange capacity, m eq per 100 g substance
	C	H	O	N	C:H	pH	
<i>Penicillium</i> (sp.)	45.2	6.1	45.9	2.8	7.4	3.26	261.0
<i>Aspergillus niger</i>	51.0	5.6	40.6	2.8	9.1	3.42	312.0
<i>Actinomyces globisporus roseus</i>	48.2	8.2	38.3	5.3	5.8	3.30	180.5

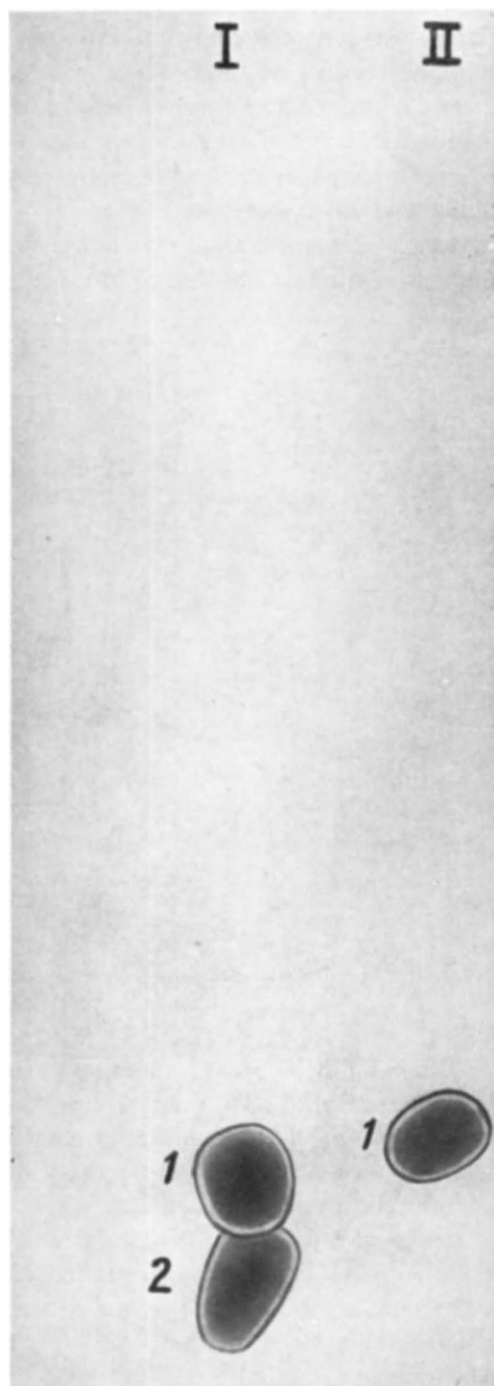


FIG. 16. Chromatogram of products of the activity of *Aspergillus niger*.

I. Products of the activity:
1. Pyrocatechol; 2. Unknown.

II. Control: Pyrocatechol.

100 g substance; excluding humus substances from *Aspergillus niger* culture solution, they are not precipitated by acids.

Newly-formed humus substances from the *Aspergillus niger* culture were hydrolysed with 6 N HCl and the amino acid composition as determined by partition paper chromatography was similar to that found for soil humic and fulvic acids (see Fig. 5).

Humus substances from the culture solution of *Actinomyces* showed a number of infra-red absorption bands (Fig. 17).

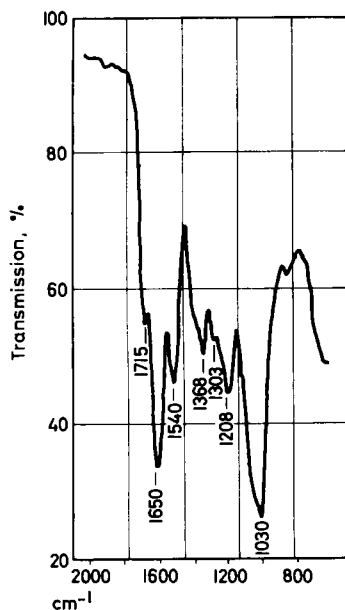


FIG. 17. The infra-red spectrum of humus substances from the culture solution of *Actinomyces globisporus roseus*.

The band at 1715 cm^{-1} ($5.83\text{ }\mu$) corresponds to the vibration of carboxyl (carbonyl) $\text{C}=\text{O}$ of aliphatic and aromatic acids. The band at 1650 cm^{-1} ($6.06\text{ }\mu$) in soil humic acids characterizes the stretching vibration of conjugated carbon double bonds, $\text{C}=\text{C}$, of aromatic structures. However the culture solution contains 5.3 per cent nitrogen and the formation of this band is possibly due to the stretching vibration of $\text{C}=\text{N}$ in heterocyclic nitrogen compounds, to the bending vibration of NH in primary and secondary amines and to the bending vibration of NH_2 in primary amides; the band at 1540 cm^{-1} ($6.49\text{ }\mu$) may also be due to these groups. The fourth band at 1368 cm^{-1} ($7.31\text{ }\mu$) can be attributed to CH_3 or CH_2

of aliphatic groups. Very pronounced bands at 1303 cm^{-1} ($7.67\text{ }\mu$), 1208 cm^{-1} ($8.28\text{ }\mu$) and 1030 cm^{-1} ($9.71\text{ }\mu$) correspond to oxygen bonds in C—O of esters, quinones and alcohols. When used to characterize the complex nature of newly-formed humus substances, infra-red spectra indicate that nitrogen-containing groups and components of an aromatic nature are present in these substances.

Judging from the work described above the humus substances formed in micro-organism culture solutions should only be regarded as initial forms of fulvic and humic acids.

It appears that during the life of micro-organisms, the formation of humus substances from the products of metabolism and resynthesis (of protoplasm components) is a common phenomenon. Results similar to ours were obtained by Mücke, Obenaus and Kipke (1959) in experiments with *Cephalosporium gordonii*. The fungus was grown on a synthetic medium containing glucose and glutamic acid; the humus substances formed in the medium contained on average 53.3% C, 6.4% H and 6.3–10.8% N. Several infra-red absorption bands were detected in them; the band at $8.1\text{ }\mu$ may be attributed to the vibration of quinone C=O.

Simonart and Mayaudon (1958) have shown that carbohydrates may take part in the formation of humus substances. They grew rye-grass in an atmosphere containing ^{14}C and subsequently isolated glucose, hemicelluloses, cellulose and other substances from the plant material. They added these substances to a soil, and in the instance of ^{14}C -labelled glucose humus substances containing ^{14}C were detected in the soil after only seven days.

It has been shown that the precursors of aromatic compounds (in particular, shikimic acid) are formed in cultures of fungi and bacteria using sugar as an energy source and this is of great interest in answering the question of whether carbohydrates take part in humus formation.

Davis (1951), Yaniv and Gilvarg (1955), and Srinivasan *et al.* (1956) have established that this occurs in experiments with *Escherichia coli* grown on a medium containing glucose, and recently Simonart and Wiaux (1960) obtained similar results with a culture of *Penicillium griseofulvum*.

It is well known that shikimic acid is genetically related to quinic acid. A number of authors have shown that micro-organisms can convert the latter into protocatechuic acid and related aromatic acids (Butkevich, 1924, 1929; Loew, Emmerling, Abderhalden and Beijerinck, see Butkevich, 1929). Consequently, during humus formation, quinic and shikimic acids may be regarded as intermediates between carbohydrates and compounds of an aromatic nature.

From the evidence quoted above, substances of a carbohydrate nature, which are decomposed mainly during the earlier stages in the humification of plant residues, may serve as primary sources of structural units in the molecules of humus substances (amino acids, proteins and polyphenol-type aromatic compounds) through diverse transformations during metabolism and resynthesis by micro-organisms.

THE ROLE OF OXIDIZING ENZYMES IN THE SYNTHESIS OF HUMUS SUBSTANCES

If the molecules of humus substances are considered to be condensation products of phenol-type compounds with amino acids and proteins, various plant substances may serve as sources of these structural units. The products of resynthesis by micro-organisms are the most likely sources of nitrogenous compounds, because most of the original nitrogen-containing compounds in plant and animal residues are easily decomposed by micro-organisms.

There are a number of sources of phenol-type compounds. They may be structural units released during the decomposition of lignins and tannins, as well as their precursors. The products of the activity and metabolism of micro-organisms utilizing various organic compounds, including carbohydrates, may also be a source of aromatic compounds.

Recent investigations have clarified the mechanism of condensation. Polyphenols commonly occur among the products of an aromatic nature which take part in the formation of humus substances. Before condensation, they are oxidized to quinones; the latter, possessing a high chemical reactivity, combine with amino acids and peptides.

Polyphenols may be oxidized to a certain extent at neutral and slightly alkaline pH (Salfeld, 1961); their oxidation to quinones proceeds easily at alkaline pH (Eller and Koch, 1920, 1926; Erdtmann, 1933, 1955). It is evident, however, that under soil conditions this mode of oxidizing polyphenols can rarely occur (for instance in microzones with increased concentration of NH_3 , or in soils with an alkaline reaction, such as solonchetses). The most important way that polyphenols are oxidized to quinones in the soil is a biochemical route, brought about by oxidizing enzymes, phenoloxidases, which are produced by many groups of micro-organisms.

Amongst early work indicating that oxidizing enzymes produced by various micro-organisms (fungi, actinomycetes, bacteria) take part in the formation of dark-coloured products, the investigations of Bertrand (1898), Beijerinck (1900), Perrier (1913) and Krainski (1914) should be mentioned.

Later investigations showed that similar phenomena occurred in cultures of *Azotobacter* (Pochon and Wang, 1950) and in a culture of *Flavobacter* grown on benzoic acid and on phenolic compounds (Treccani-Benetti and Schiesser, 1950).

A number of authors have recently established that dark-coloured condensation products are formed from phenols in the presence of phenol-oxidases produced by fungi and actinomycetes (Flaig, 1952; Küster, 1953, 1955, 1956; Freudenberg *et al.*, 1943, 1955; Hofmann, 1955; Lindeberg, 1955; and others).

We have observed similar effects in experiments in which condensation of polyphenols took place in the presence of enzymes produced by micro-organisms: fungi, cellulose-decomposing myxobacteria, and actinomycetes. The experiments were laid out as follows.

Microbes were carefully removed from a culture of vigorously growing organism by filtering and centrifuging and the presence of phenoloxidase was established by qualitative test. Mixtures were prepared of the substances whose reactions were to be tested, and to each mixture was added some culture solution, phosphate buffer, 1% H_2O_2 and a few drops of toluene. The mixtures were placed in a thermostat at 25–30° C. Condensation of the substances in the mixture was indicated by the appearance of a brown colour, which was used to estimate the intensity of the process, either colorimetrically or by determining the extinction coefficient E .

The same mixture, in which the culture solution had been inactivated by heating for 10 minutes in boiling water, was used as a control.

Results from several experiments are given below.

Experiment 1. *Oxidation and condensation of aromatic compounds in the presence of phenoloxidase produced by cellulose myxobacteria*

The following mixtures were prepared:

1 % solution of investigated substance	2 ml
Phosphate buffer, pH 5.9	2 ml
Culture solution	2 ml
1 % H_2O_2	0.5 ml

The intensity of the process is shown in Fig. 18.

An interesting fact came to light: only those compounds possessing hydroxyl groups (OH) in the *ortho* and *para* position, and therefore liable to direct conversion into quinones, were rapidly oxidized (Fig. 18).

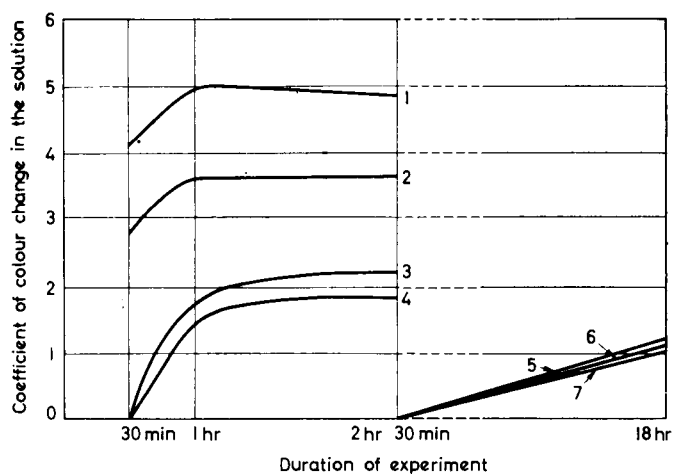
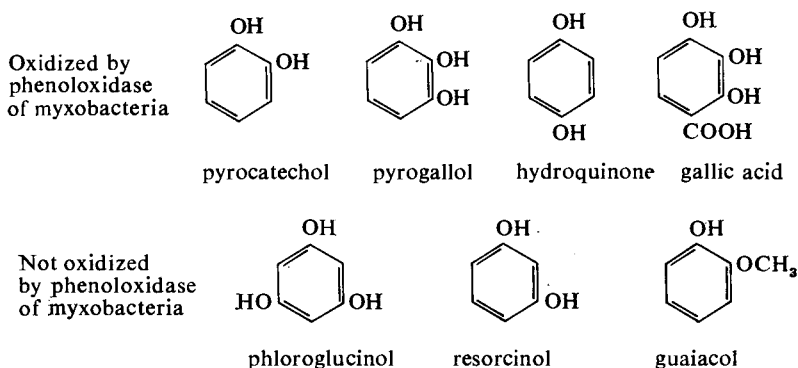


FIG. 18. The oxidation of various aromatic compounds by phenoloxidase of cellulose myxobacteria.

1. Pyrogallol; 2. Gallic acid; 3. Hydroquinone; 4. Pyrocatechol; 5. Guaiacol (1·12); 6. Resorcinol (1·10); 7. Phloroglucinol (1·08).



Experiment 2. *The participation of oxidizing enzymes of cellulose myxobacteria in the condensation of polyphenols with proteins*

Having established that phenoloxidase is present in cellulose myxobacteria, we decided to check the correctness of our hypothesis that oxidizing enzymes of cellulose myxobacteria are biocatalysts in the condensation of polyphenols with proteins.

With this in mind, we carried out some experiments in which pyrogallol and soluble peptone mixtures were allowed to condense in the presence of the liquid from a cellulose-myxobacteria culture.

For this experiment a mixture of the following composition was prepared:

Pyrogallol	1 g dissolved in 15 ml water
Soluble peptone	0.5 g dissolved in 30 ml water
Phosphate buffer, pH 5.9	10 ml
Culture liquid of cellulose myxo- bacteria	10 ml
1% H_2O_2	3 ml

For the control, the same mixture, but with sterilized culture medium, was used. The mixture was left for 18 hr in a thermostat at a temperature of 25–30° C in the presence of toluene. During this period the mixture which contained the culture liquid became strongly turbid and darkened; in the controls the mixture changed only slightly.

After the addition of a few drops of 10 per cent H_2SO_4 large amounts of a brown amorphous precipitate were formed in the flasks, but only very small amounts in the control flasks. After heating for a short time on a water-bath, the precipitate was separated by centrifuging, washed free from surplus reagents and dissolved in 0.1 N NaOH. After the addition of 1 N H_2SO_4 a dark brown gel precipitated and SO_4^{--} were removed by washing with water. The preparations were then dissolved in an equal volume of 0.1 N NaHCO_3 and the solutions were examined in a Pulfrich spectrophotometer.

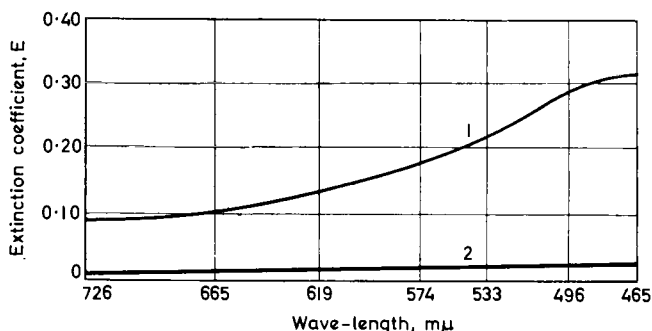


FIG. 19. Condensation of peptone and pyrogallol.

1. Peptone + pyrogallol, enzyme +; 2. Peptone + pyrogallol, enzyme --.

As can be seen from Fig. 19 the values for the extinction coefficient (E) were extremely low when a reaction occurred between peptone and pyrogallol in the absence of enzymes (sterilized culture liquid). Where enzymes

were present (active culture liquid) the condensation reaction proceeded very intensively.

Similar results were obtained where gelatin or albumen was used instead of peptone. However, where glyocoll was used the reaction was slight.

Experiment 3. *The condensation of pyrogallol with decomposition products of the plasma of cellulose myxobacteria*

This series of experiments aimed at showing whether or not decomposition products of the plasma of cellulose myxobacteria are components in the formation of the humic-acid molecule. Since the plasma of these micro-organisms, according to chemical analyses (see Table 26), contains up to 75 per cent proteins (with 12 per cent N), it is quite probable that decomposition products of the plasma may serve as the nitrogenous component for a condensation with polyphenols.

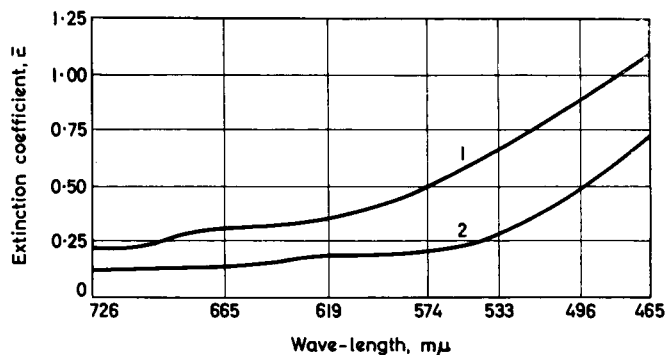


FIG. 20. Condensation of the decomposition products of myxobacterial plasma and pyrogallol.

1. Enzyme +; 2. Enzyme -.

The decomposition products of cellulose myxobacteria were obtained as follows: the slimy bacterial mass was removed from the surface of the solid starch-ammonia medium in Petri dishes; this was spread out in a thin layer on glass for rapid drying and then ground to a powder. A 1 g sample of this substance was moistened with water and kept in a thermostat at 40° in the presence of toluene. After 24 hr the mixture was diluted with a small amount of water, shaken, and centrifuged. The resulting liquid was then separated from the precipitate by decantation and used in place of the peptone solution. Otherwise, the arrangement of the experiment was as before.

The experiment gave positive results: with the replacement of peptone by decomposition products of myxobacterial plasma condensation products were formed, the reaction being noticeably more intense in the active culture liquid. Evidence of this was provided by the higher values of the extinction coefficient (E) of solutions of the condensate compared with the control (Fig. 20).

Experiment 4. *Condensation of pyrogallol with peptone in the presence of phenoloxidase from Aspergillus niger*

The experimental arrangement was similar to that in Experiment 2, except that the condensation of pyrogallol and peptone was carried out with the addition of culture solution from *Aspergillus niger*, which contained active phenoloxidase.

Figure 21 shows the importance of this enzyme in the condensation.

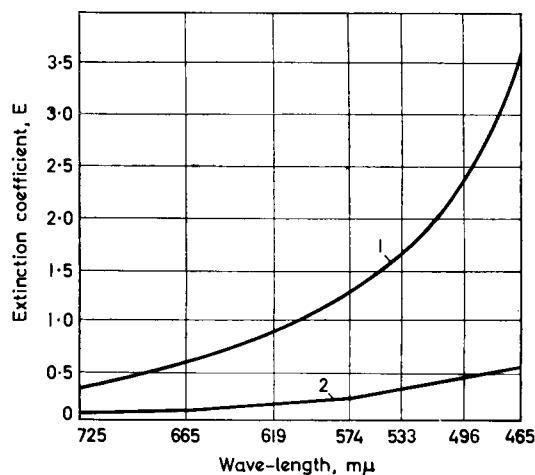


FIG. 21. Condensation of peptone and pyrogallol in experiment with *Aspergillus niger*.

1. Peptone + pyrogallol, enzyme + 2. Peptone + pyrogallol, enzyme —.

Experiment 5. *Condensation of pyrocatechol with lysine in the presence of phenoloxidase from Aspergillus niger*

The experimental conditions were similar to those in Experiments 3 and 4 except that pyrocatechol and lysine (0.5 g each) were the reacting components. Figure 22 shows that the condensation of pyrocatechol and lysine is considerably activated by the presence of phenoloxidase.

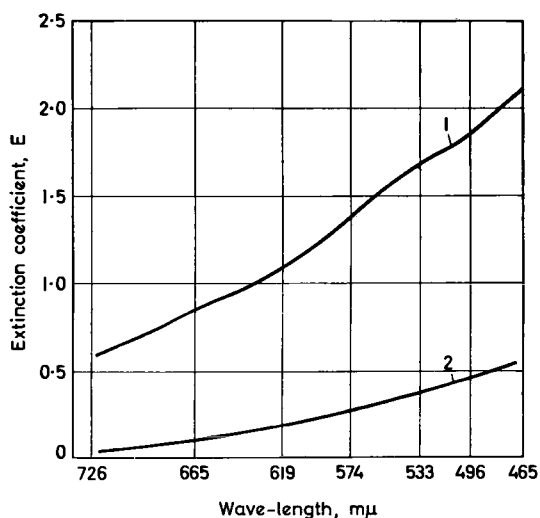


FIG. 22. Condensation of lysine and catechol in experiment with *Aspergillus niger*.
1. Lysine + catechol, enzyme +; 2. Lysine + catechol, enzyme -.

A number of investigations have shown that laccase takes part in polyphenol oxidation. Amongst other oxidizing enzymes, laccase was detected by Flaig (1961) in the culture solution of *Polystictus versicolor*; polyphenols were oxidized by this enzyme in various ways. In the presence

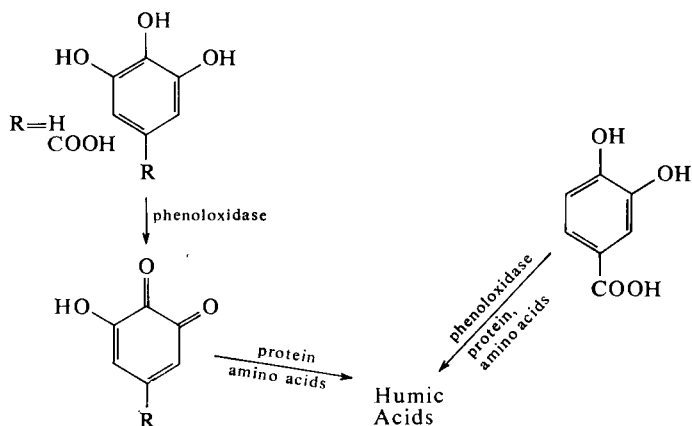


FIG. 23. Scheme for the oxidation of polyphenols and subsequent condensation with protein (or amino acids) during formation of humic acids (Flaig, 1960).

of laccase produced by this fungus, Trojanowsky (1961) obtained dark-coloured condensation products in mixtures of catechol or hydroquinone with amino acids and glucose.

Various forms of polyphenol oxidation, with subsequent condensation of the oxidized products are discussed by Flaig (1958b, 1960), and Flaig and Haider (1961). One of the possible schemes is given in Fig. 23.

It appears that an intermediate stage in the transition to polymerized products (Fig. 24) is the formation of dimers from double aromatic rings (Forsyth and Quesnel, 1957).

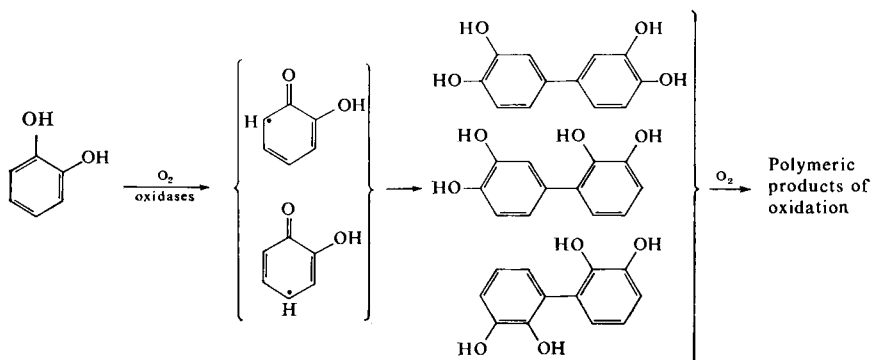


FIG. 24. Scheme for the oxidation of polyphenols and the formation of polymer products (Forsyth and Quesnel, 1957; see Flaig and Haider, 1961).

Flaig (1960) points out that monophenols and monophenol carboxylic acids may also take part in condensation reactions in the following way. A new hydroxyl group is introduced into these compounds, in the ortho-position to the hydroxyl already present, and then by the action of microbial oxidases, the products are dehydrogenated, and via quinones and dimers, polymerized.

All this work indicates the diversity of ways by which humus substances may be formed when plant residues are humified; we have attempted to show this schematically in Fig. 25. The fundamental idea of the scheme is as follows. Any plant substances may, by complex transformations, take part in forming humus substances. At the same time, any plant substances, including resistant lignin, may be decomposed to a greater or lesser degree by micro-organisms to the final products of mineralization; in this case, they contribute very little to the formation of humus substances.

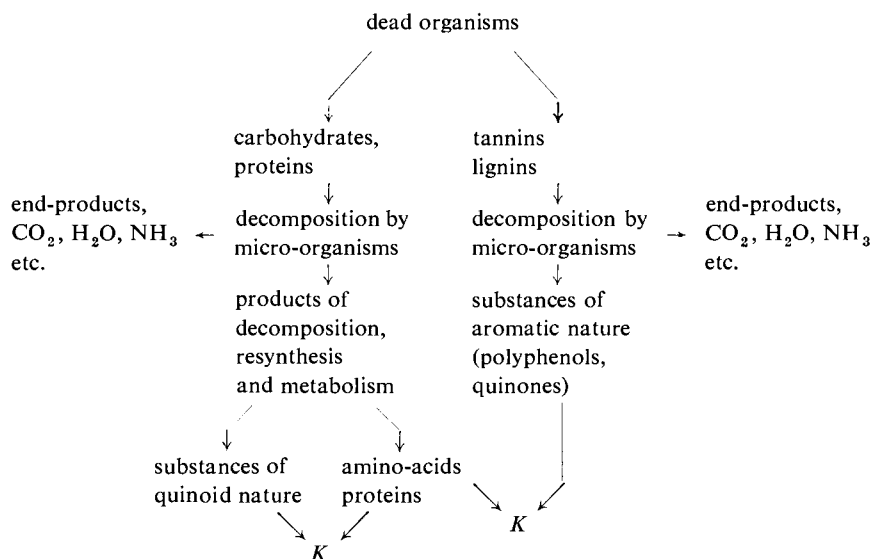


FIG. 25. Possible ways of forming humus substances during the humification of plant residues. *K* = condensation.

All this indicates new humus substances are formed when the biological activity is intense. Micro-organisms fulfil many functions in this process:

1. They decompose original plant (and animal) residues into simpler compounds, including those which subsequently serve as structural units in the molecules of humus substances (for instance, "structural units" of lignin, tannins, etc.).

2. The products of microbiological resynthesis and metabolism (amino acids, proteins, amino sugars, various compounds of an aromatic nature and their precursors) take part as structural units, in forming molecules of humus substances.

3. The role of micro-organisms in humus formation is further increased by the fact that under soil conditions, polyphenols are for the most part biologically oxidized to quinones by phenoloxidases produced by numerous groups of micro-organisms (fungi, actinomycetes, bacteria).

THE FORMATION OF HUMUS SUBSTANCES OF MELANOIDIN TYPE

In previous sections the ways of forming humus substances with aromatic structures were examined. There is, however, no doubt that melanoidin-type humus substances can also be formed.

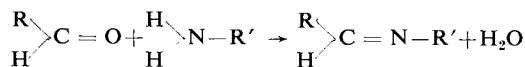
As is well known, melanoidins are formed in many technological processes. In some of them the formation of melanoidins is essential for obtaining high quality products (e.g. bread baking, malt production, beer); in others, the formation of melanoidins is undesirable (e.g. production of sugar and alcohol).

Maillard, in early work (1912, 1913, 1916, 1917), showed that dark-coloured amorphous products containing nitrogen were formed when amino acids and reducing sugars interacted at elevated temperatures; these products he called melanoidins. Such substances were obtained from mixtures of glycine and glucose, and glycylglycine and xylose. According to Maillard, melanoidins are formed when the NH_2 groups of amino acids interact with aldehyde or keto groups in sugars.

There have been a number of subsequent studies of the mechanism of melanoidin formation. Melanoidins, prepared by Enders and Theis (1938) from glycine and glucose, were sparingly soluble in water and dilute acids, but easily dissolved in alkali solution from which they were precipitated as a gel by acidification. In this respect they behaved like humic acids. The preparations contained hydroxyl, carbonyl and carboxyl functional groups and consequently possessed acidic properties. It is interesting that Enders and Theis detected phenolic groups in these preparations obtained from aliphatic substances; this may possibly be explained by the formation of some intermediate forms transitional to aromatic compounds.

Enders (1943a, b) noted the important role of melanoidins, formed by the reaction of methylglyoxal with amino acids, in the composition of soil humus. This is regarded by Schuffelen (1950) as a possible way of forming humus substances.

It is now considered that melanoidins are formed by a complex oxidation-reduction process accompanied by the formation of intermediate products. In the first stage, a Schiff's base reaction occurs between amino compounds and the carbonyl groups:



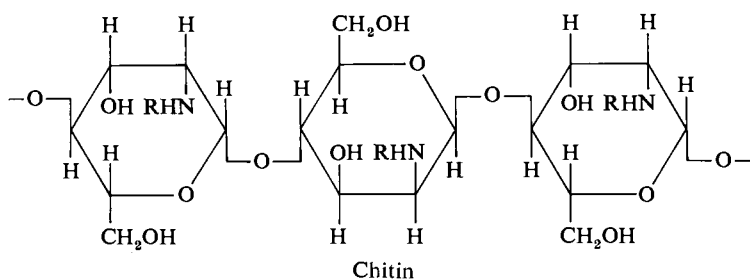
In this process, furfural and hydroxymethylfurfural are formed and also "reductones", compounds containing the ene-diol group, as in ascorbic acid, and having a tendency to aromatization (Kretovich and Tokareva, 1948; Manskaya, Drozdova and Tobelko, 1954; Drozdova, 1957, 1959b; Smirnov and Geispiets, 1956).

It is now clear that melanoidins are formed not only at elevated

temperatures but also at 30–35° C (Drozdova, 1959b); their formation is therefore quite possible in the soil.

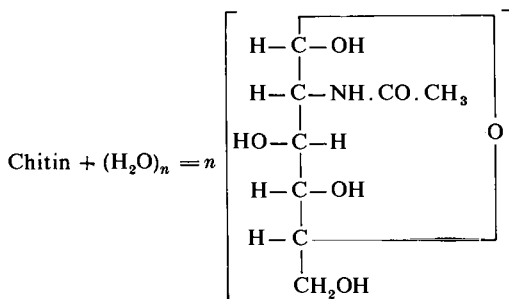
Because the carbohydrate and amino acid components of plant residues may be rapidly decomposed, it is unlikely that melanoidins are formed in the soil from these substances. Apparently the most likely sources of melanoidins in the soil are amino sugars of microbial origin and also chitin, which consists of nitrogen containing acetyl glucosamine residues, linked to each other by β -glucosidic bonds.

Chitin occurs widely in nature as a component of fungi (*Basidiomycetes*, *Fusarium*, *Penicillium* and *Aspergillus*) and lichens. Crustacea, arachnida and also some species of coelenterata and molluscs have chitin shells and skeletons.



A large accumulation of chitin is not found in the soil, in spite of its regular addition as a component of dead plants and animals and of the shells shed annually by animals. This may be because it is utilized by microorganisms; Bremner (1954) has shown that microbes can decompose chitin and glucosamine. In the first step, chitin is oxidized by an enzyme, chitinase, the presence of which has been established in many plant and animal organisms (in fungi, lichens, earthworms, amoeba, etc.). Bacteria decomposing chitin have been isolated from soils, subsoils and sea water (Veldkamp, 1952; Gehring, 1955; Sreenivasan, 1955; Clarke and Tracey, 1956).

Drozdova (1957) has thoroughly investigated the formation of melanoidins from chitin; she concluded that the process begins with the enzymic decomposition of chitin to N-acetylglucosamine and glucosamine, which easily form Schiff's bases or N-glucosides. These substances may be directly converted via pyrazines to melanoidins. This is accompanied by the formation of intermediate products: furfural, hydroxymethyl-furfural, other aldehydes, reductones and some other substances, which by reacting with amino compounds or NH_3 take part in melanoidin formation.



From this account, it may be considered that melanoidin-type humus substances are formed under soil conditions on a much larger scale than as hitherto been recognized. For instance, Capriotti (1961) observed that soluble melanoidins are formed by streptomycetes in a nutrient medium containing gelatin and glucose. The condensation of uronic acids with amino acids exuded by living plants may be one of the ways that melanoidins are formed in the soil (Rudakov, 1949). Specific humic acids of the melanoidin-type, in which no aromatic groups could be detected by infra-red spectroscopy, were isolated from sapropels by Karavaev and Udyak (1960).

THE DECOMPOSITION OF HUMUS SUBSTANCES BY MICRO-ORGANISMS

In spite of their complex structure, humus substances can be utilized to a greater or lesser extent by micro-organisms. This may be seen from the appearance of fungi and colonies of micro-organisms on humic acid salts and also in solutions of humates and fulvates, as noted by Nefedov (1897), Slezkin (1900), Reinitzer (1900) and others.

Nikitinskii (1902) inoculated media containing humic acid and found that fungi and bacteria can utilize humic acid as a source of nitrogen.

Subsequent work (Pontovich, 1938; Dikussar, 1945; Kudrina, 1951; Aleksandrova, 1953b; Küster, 1952b; Ambroz, 1956; Didier, 1956; Volkova, 1961; Schönwälder, 1958; Burges and Latter, 1960) showed that humic acids are utilized by different groups of micro-organisms: fungi, actinomycetes, yeasts, sulphate-reducing thermophilic bacteria and others.

However in all the cited work, the micro-organisms apparently utilized only organic impurities in the humic acid preparations or side chains

of the humic acid; clarification of the medium, indicating cleavage of the humic acid nucleus, was not observed.

Nevertheless, micro-organisms can utilize substances of an aromatic nature. In the section dealing with the part played by lignin in the formation of humic acids, we referred to the investigations of Stanier, Evans and Kilby and others, who established that oxidation of lignin structural units can be terminated by cleavage of the ring, leading to the formation of low-molecular-weight organic acids, such as β -keto-adipic acid. Certain species of *Pseudomonas* play an active part in this process.

Soil micro-organisms (proactinomycetes, myxobacteria, fungi) can use heterocyclic nitrogen compounds (pyridine, pyrrole, etc.) as nitrogen sources (Küster, 1952b).

Returning to the utilization of humus substances by micro-organisms, it should be mentioned that under soil conditions, the decomposition of humus substances is favoured by two factors. Firstly, humus substances do not occur in the form of purified compounds, but in a mixture with other organic substances, which include those easily decomposed by micro-organisms; secondly, humus substances are subject in the soil to the action of associations of micro-organisms with different inherent functions. This second point was particularly stressed by Vinogradskii (1952), who pointed out that the activity of autochthonous micro-flora in the soil is directed towards the oxidation of humus substances, their sole source of energy. Advanced decomposition of humus substances by the action of micro-organism complexes may be inferred from the work of Lazarev (1939, 1949) and co-workers, Bylinkina (1949), Mityushina (1950) and Movchan (1958): when soil crumbs or a soil suspension were distributed on the surface of the gel containing humate, zones of clarification were observed.

A number of recent investigations have indicated that the rate of decomposition of humus substances is increased when organic compounds easily utilized by micro-organisms are added. Thiele and Andersen (1953) observed a similar effect when humic acids were decomposed in the presence of glucose or proteinaceous substances. Mishustin, Nikitin and Ochilova (1960) and Mishustin and Nikitin (1961) have established that when carbohydrates and nitrogen in forms easily available to micro-organisms were added to a nutrient medium containing humate which had been inoculated with *Pseudomonas fluorescens*, the medium was completely decolorized. According to the authors, this shows that the aromatic rings of humic acid were destroyed; this phenomenon is associated with the presence of highly active catalase and peroxidase in bacteria which decompose humic acids (Nikitin, 1960).

Fedorov and Il'ina (1961) observed a similar phenomenon when they added glucose to a nutrient medium containing humic acid which was inoculated with actinomycetes.

A number of authors (Broadbent and Norman, 1946; Broadbent, 1948; Bingeman *et al*, 1953; Pinck and Allison, 1951; Hallam and Bartholomew, 1953; Barrow, 1960; Jenkinson, 1962; Turchin *et al*, 1962) have shown, by using ^{14}C and ^{15}N -labelled plant material, that it is possible to increase the rate of decomposition of soil humus when easily-decomposable plant material is added to the soil. However, some authors consider that this effect is insignificant (Pinck and Allison, 1951; Mortensen, 1963).

Accelerating the decomposition of soil humus by adding organic matter easily available to micro-organisms is mainly of practical importance for soils rich in stable forms of humus (peaty soils, chernozems); Tyurin and Mikhnovskii (1961) and Rybalkina and Kononenko (1961) give data which support this practice.

HUMUS FORMATION IN PLANT TISSUE

Experimental procedure

Experiments with isolated plant substances can be regarded merely as supplementary, revealing different aspects of the process. With this in mind we carried out experiments on the humification of plant residues which we shall now describe.

The residues of grass vegetation (grasses and legumes)—which are the main source of humus substances (particularly in cultivated soils)—served as the objects of our investigations. Roots of lucerne and clover, clover leaves and roots of *Agropyron tenerum* and timothy were used. Some observations were also made with hazel leaves and Scots-pine needles.

The experiments were carried out under laboratory conditions, in composts with or without soil, kept at optimum moisture conditions and at a temperature of 25–28° C. The roots were cut into portions 2–3 cm in length; the leaves were left whole.

Bearing in mind the need for a more detailed study of the character of the changes occurring in plant residues during humification and the obvious inadequacy of chemical group-analysis alone for this purpose, we adopted a combined study of the chemical composition and anatomical structure of the plant residues. In addition, the nature and properties of the newly-formed humus substances were studied.

Apart from the laboratory experiments, we succeeded in making comparative observations on the decomposition of the same plant materials in different soil-climatic zones—podzolic, chernozem, chestnut and serozem soil zones. Long-term observations under laboratory and field conditions enabled us to establish a number of general regularities, the main points of which are discussed in this chapter.

Nature of the changes in plant residues during humification

Under optimum temperature conditions and adequate moisture, plant residues are subject to the action of various groups of micro-organisms. A study of the numbers and composition of the microflora taking part in the humification of lucerne and grass roots was carried out by Krasil'nikov and Nikitina (1945) and also by Mishustin and Timofeeva (1944). In experiments parallel to ours, they observed the following sequence of changes in the microflora: in the early stages of composting an intensive

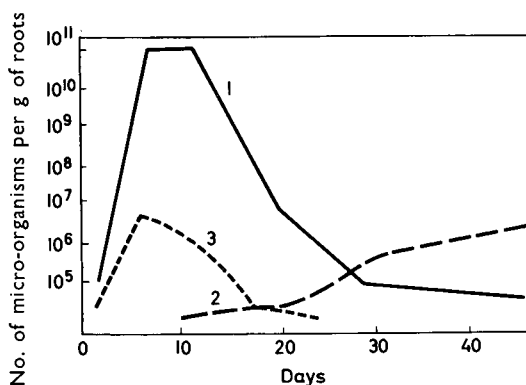


FIG. 26. The composition of the microflora in experiments on the decomposition of plant residues (Krasil'nikov and Nikitina, 1945).

1. Bacteria; 2. Actinomycetes; 3. Fungi.

development of mould fungi and different types of non-spore-forming bacteria was observed, the latter being replaced later by spore-forming types. After a certain time the number of bacteria decreased markedly and at the end of the process an increased number of actinomycetes was observed (Fig. 26).

At a time when a reduction in the growth of non-spore-forming bacteria had occurred Mishustin and Timofeeva observed an extremely intensive development of cellulose bacteria. Though these investigations are far

from complete and have not included the whole diversity of micro-organisms taking part in the humification of plant residues, the following sequence of changes in the main groups of micro-organisms can, however, be recorded:

mould fungi and non-spore-forming bacteria → spore-forming bacteria → cellulose myxobacteria → actinomycetes

The development of different groups of micro-organisms is determined to a large degree by the composition of the plant residues. Thus, mould fungi and saprophytic bacteria, which develop at an early stage of humification, utilize the most readily available organic substances (carbohydrates, amino-acids, simple proteins and the readily decomposable part of cellulose). The saprophytic microflora is then replaced by specific groups including cellulose myxobacteria. As already mentioned, the latter have a capacity for utilizing different carbohydrates, but the fact that they can only assimilate inorganic forms of nitrogen explains why a mass development of myxobacteria is possible only when inorganic nitrogen formed by mould fungi and saprophytic bacteria appears in the medium. However, these groups utilize the most readily available part of the carbohydrate components of plant residues. Therefore, although cellulose myxobacteria have the capacity for assimilating various carbohydrates, they utilize mainly cellulose and also, apparently, inter-cellular hemicelluloses, depending on the ecological conditions.

At the end of the process of humification of the plant residues a vigorous development of actinomycetes is observed; compared with other groups of micro-organisms the latter are more capable of utilizing difficultly decomposable components of plant tissues and also newly formed humus substances.

Naturally, the given scheme showing the change in the microflora during the humification process can only be regarded as approximate. The decomposition of plant residues is brought about by a complex of various micro-organisms, whose composition depends on the chemical composition of the plants and the conditions under which decomposition takes place (Raznitsyna, 1947; Tepper, 1949; Rȳbalkina and Kononenko, 1959).

As a result of the activity of the various groups of micro-organisms the tissues of plant residues lose their coherence and the residues become unstable and decrease in volume and weight; this suggests that during humification a partial mineralization of organic substances to end-products (CO_2 , H_2O , etc.) takes place.

During humification the plant residues become brown in colour and after a certain time, if sufficient moisture is present, a brown liquid, which is an aqueous solution of humus substances, can be expressed from them.

At fixed conditions of temperature and moisture, the changes in the plant residues occur at rates depending on the chemical composition of the residues.

Thus, the first signs of humification and the appearance of humus substances were recorded after the following intervals (days):

	Clover leaves	Clover and lucerne roots	<i>Agropyron tenerum</i> roots	<i>Agropyron cristatum</i> roots	Hazel leaves	Scots-pine needles
The beginning of visible changes	2-4	5-8	20-30	20-25	5-8	30-35
The first appearance of humus substances	14-20	60-75	180-200	180-200	25-30	120-180

Humification was most rapid in the leaves and roots of legumes (clover and lucerne) and in the leaves of woody species, and was slowest in perennial-grass roots and Scots-pine needles.

Judging from the character of the changes, humification was completed in 2-3 weeks in clover leaves and $2-2\frac{1}{2}$ months in clover roots and lucerne roots; in grass roots the humification process took much longer (Table 28).

TABLE 28. CHANGE IN WEIGHT OF PLANT RESIDUES DURING HUMIFICATION AS PERCENTAGE OF ORIGINAL WEIGHT

Materials investigated	Duration of the experiment (days)								
	5	10	15	30	60	75	120	180	300
Clover leaves	60-70	55-60	35-40	30	30	—	25-30	—	—
Roots of clover and lucerne	80-90	60-70	—	—	—	30-40	—	25-40	—
Timothy roots	changes negligible	90	85	80	—	60	55	50	
Hazel leaves	—	70	—	53	48	—	38	—	—
Scots-pine needles	changes negligible	—	74	—	—	48	35	—	
<i>Agropyron tenerum</i> roots	changes negligible	—	90	86	—	—	53	53	

From the data of Table 28 showing the loss in weight of plant residues, it is possible to calculate the humification coefficient, i.e. the approximate amount of humus corresponding to the original amount of plant substances. Taking the final loss in weight as a result of mineralization to be approximately 50–70 per cent it can be assumed, correspondingly, that the humification coefficient is 0.3–0.5. Similar values for the humification coefficient of various plant residues and farmyard manure were given by Hénin and Dupuis (1945) and Jacquin (1962). We have used humification coefficients for calculating the balance of organic matter in cultivated soils (see Chapter 7).

Changes in the chemical composition of plant residues during humification

To obtain a general picture of the decomposition of different groups of plant substances during humification, we determined the chemical composition of fresh and humified plant residues employing the usual scheme of plant analysis as presented by Kizel' (1934). The protein content was calculated by multiplying the total nitrogen content by 6.25, and the lignin content from the amount of residue remaining after hydrolysis with 72 per cent H_2SO_4 (Table 29).

TABLE 29. CHEMICAL COMPOSITION OF NON-HUMIFIED PLANT RESIDUES, AS PERCENTAGE OF ABSOLUTE DRY ASH-FREE MATERIAL

Materials investigated	Substances extractable with ethanol-benzene	Starch	Hemi-celluloses	Cellulose	Protein N \times 6.25	Lignin residue	Total
Clover leaves	23.07	3.00	8.07	15.40	21.67	4.29	75.5
Lucerne roots	11.24	17.75	11.94	20.97	13.31	8.61	83.82
Timothy roots	5.26	2.25	20.35	25.91	7.75	19.54	81.06
<i>Agropyron tenerum</i> roots	6.97	none	22.86	25.49	7.94	18.43	81.69
Scots-pine needles	24.47	none	12.68	27.59	6.97	15.05	86.76

The data of Table 29 show that the plant residues used in the experiment differed fairly widely in chemical composition. Thus, clover leaves and lucerne roots had a relatively high protein content (21.67 and 13.3 per cent

respectively) and a low lignin content (4.29 and 8.6 per cent). On the other hand, grass roots (timothy and *Agropyron tenerum*) had a low protein content (about 8 per cent) and a relatively high lignin content (18–19 per cent). In clover leaves hemicelluloses and cellulose were present in small amounts (totalling about 23 per cent); in the other cases the content of these substances was 30–50 per cent. Reserve substances (starch) were only present in significant amounts in lucerne roots. In Scots-pine needles and clover leaves a large amount of substances extractable with ethanol-benzene mixture was found; in the former these appeared to be mainly resinous substances and in the latter mainly chlorophyll. The intensity of humification of the various plant residues is determined to a considerable degree by the ratio between these groups of substances. The composition of humified plant residues is given in Table 30.

TABLE 30. CHEMICAL COMPOSITION OF HUMIFIED PLANT RESIDUES AS PERCENTAGE OF ABSOLUTE DRY ASH-FREE MATERIAL

Materials investigated	Substances extractable with ethanol-benzene	Starch	Hemi-celluloses	Cellu-lose	Protein N \times 6.25	Lignin residue	Total
Clover leaves	15.58	none	5.52	13.20	34.24	15.70	84.24
Lucerne roots	2.54	1.44	13.46	14.81	20.70	33.16	86.11
<i>Agropyron tenerum</i> roots	3.35	none	17.90	16.12	16.37	32.40	86.14
Scots-pine needles	8.36	none	13.56	10.00	—	37.20	—

A comparison of data on the chemical composition of humified and non-humified residues shows that the percentage of material extractable with ethanol-benzene, and also the percentages of starch, cellulose and hemicelluloses, decrease greatly during humification while the amounts of protein and lignin increase.

In addition, we calculated the amount of these substances in the residue remaining (Fig. 27).

The greatest losses were found in the following groups: starch, cellulose and substances extractable with ethanol-benzene. With hemicelluloses and proteins the losses were considerably smaller, which is attributable to the secondary synthesis of these substances in the form of microbial plasma.

The most stable substance was lignin, the content of which decreased very little.

From these data an interesting fact is revealed (cf. Tables 28, 29, 30): the higher the content of easily mobile substances and the lower the content of lignin the more rapidly are the plant residues humified. Thus, of all the materials studied, clover leaves were the most rapidly humified and grass roots were the slowest to humify.

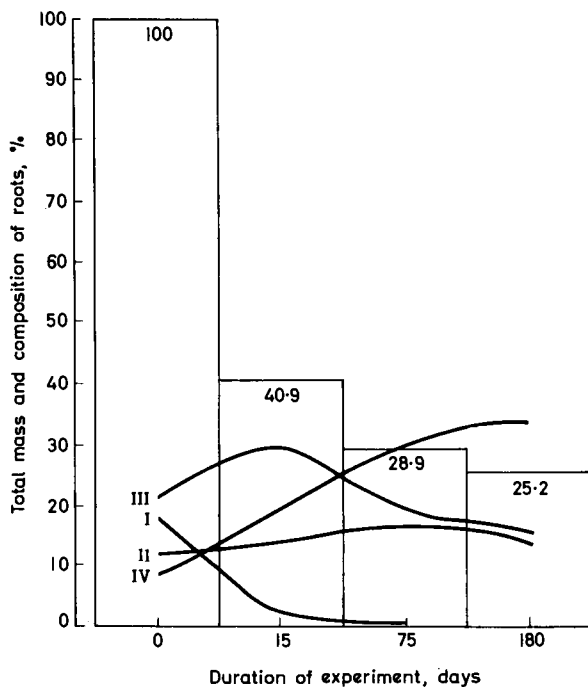


FIG. 27. Change in the chemical composition of lucerne roots during humification (M. M. Kononova).

I. Starch; II. Hemicelluloses; III. Cellulose; IV. Lignins.

Our results characterizing the intensity of decomposition of the individual groups of plant substances were, in general, similar to those obtained by many of the investigators already mentioned in the discussion of the lignin and cellulose theories on the origin of humic acids.

It was not clear from a review of these works or from our own data which of the components of plant residues participate in the formation of humus substances—those intensively decomposed during humification

(carbohydrates, proteins), or those more resistant to decomposition (lignin). In finding an answer to this problem a study of the anatomical structure of the residues was of considerable value.

Changes in the anatomical structure of plant residues during humification

The anatomical structure of fresh and humified roots was studied with preparations made according to Strasburger (1923) and Naumov (1932). The preparation of microtome sections presented no difficulty and we succeeded in obtaining sections 16–18 μ in thickness. With these sections a number of microchemical tests were carried out: for cellulose (Cl Zn I test), starch (I in KI), protein (biuret reaction) and lignin (phloroglucinol and HCl). Some of the sections were made into permanent preparations by embedding them in a mixture of glycerine and gelatin.

A study of the anatomical structure of leaves was carried out by direct microscopic examination of the individual tissue sections.

The authenticity and reproducibility of our results have been confirmed by Belyakova (1957), Remezov and co-workers (1959) and Kullmann (1959), who found by microscopic observation the same sequence of decomposition in the root and leaf tissue of perennial grasses and in the leaves of trees, as we observed in our experiments.

The following data were obtained from numerous observations on plant residues decomposing under laboratory and field conditions.

Lucerne roots (Kononova, 1943). We shall examine first the structure of living lucerne roots (Fig. 28).

The root is covered externally by periderm (per) internal to which is situated the primary cortex (pc) consisting of spongy parenchyma whose cell walls show a distinct reaction for cellulose. Internally, there is a clearly defined phloem (phl), which consists of sieve tubes serving for the translocation of plastic substances from the stem to the root, phloem parenchyma and bast fibres (bf). The walls of the sieve tubes show a positive reaction for cellulose while the walls of the bast fibres are slightly lignified and so give a positive reaction with phloroglucinol and HCl. Internal to the phloem is the cambium (cam) which forms phloem peripherally and xylem internally. The cambium gives a positive reaction for protein (biuret test).

In the wood, medullary rays (mr) containing starch grains, woody fibres (wf) and water-conducting xylem vessels (x) whose lignified walls are stained a bright red by phloroglucinol and HCl are clearly distinguishable. The photomicrograph (Fig. 29) shows a section of the xylem with xylem vessels, wood fibres and medullary rays.

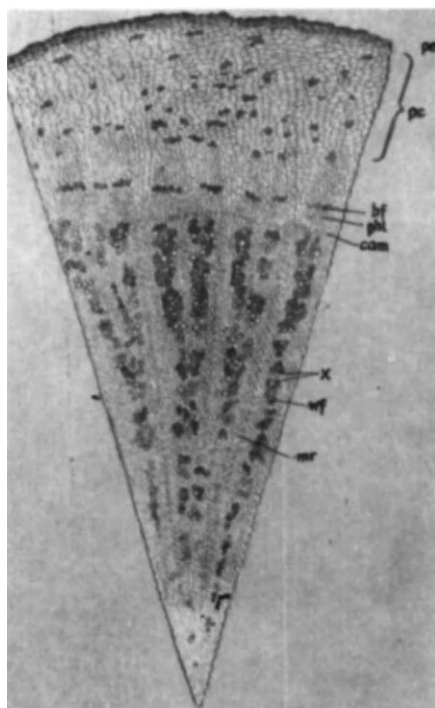


FIG. 28. The structure of unhumified lucerne root.



FIG. 29. A section of the xylem of lucerne root ($\times 270$).

The decomposition of lucerne root begins in the primary cortex and medullary rays, the latter disappearing completely, together with their contents. The cambium and primary cortex are also rapidly decomposed as can be seen from Fig. 30, which shows a section of the root after a decomposition period of 15 days.

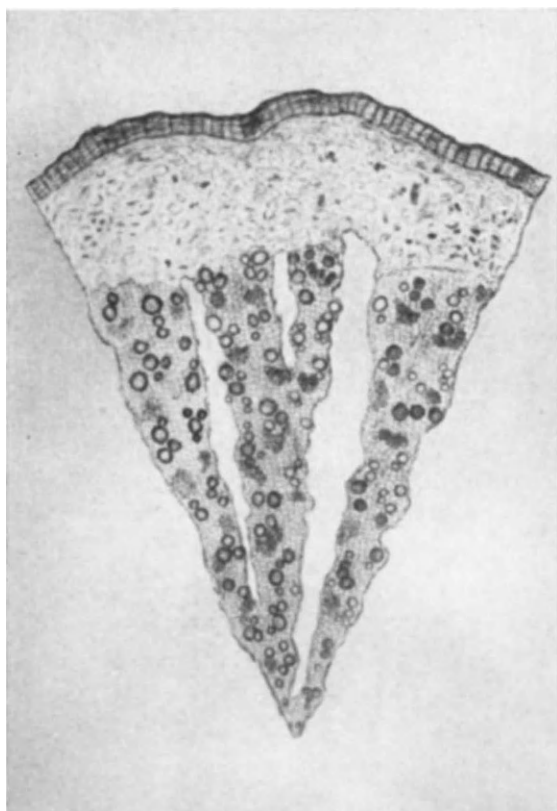


FIG. 30. The structure of lucerne root at an early stage of humification (15 days).

Thus, the first to be decomposed are living tissues with rich internal contents, namely, starch-containing medullary rays, cambium, phloem and parenchyma of the primary cortex. The formation of humus substances has not been observed during the decomposition of these tissues in plant residues; it appears that during its initial stages decomposition proceeds for the most part to end-products of mineralization, which accounts for the great loss in weight of lucerne roots (Table 28).

Later, the decomposition of wood parenchyma in the xylem begins (Fig. 31).

An examination of individual tissue sections revealed an interesting phenomenon—the presence in the tissues of enormous numbers of bacteria similar in appearance, which after isolation and study were found to be

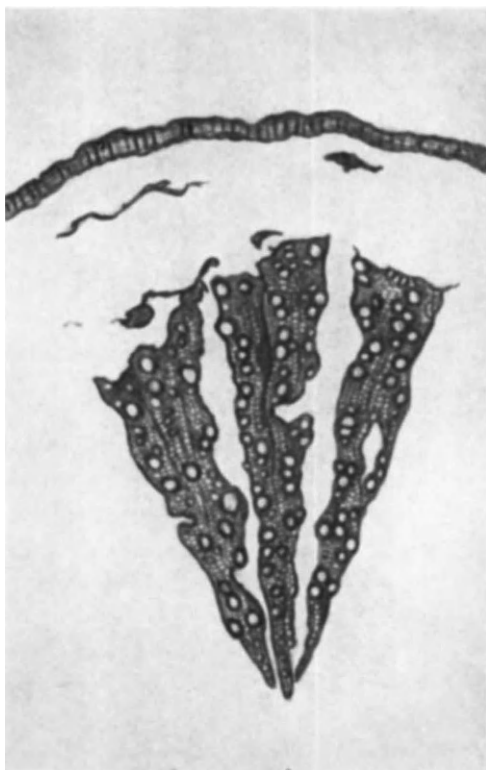


FIG. 31. The humified root of lucerne.

cellulose myxobacteria. The photomicrograph (Fig. 32) shows a section of the xylem of lucerne root with water-conducting vessels and adjacent parenchyma. The latter has lost its structure and is completely filled with bacteria which have also penetrated into the interior of the vessels. The walls of the vessels, however, remain intact at this stage of humification and, as previously, they give a positive reaction with phloroglucinol and HCl.

Under favourable moisture and temperature conditions these phenomena are observed within 1–2 months of the beginning of the experiment.

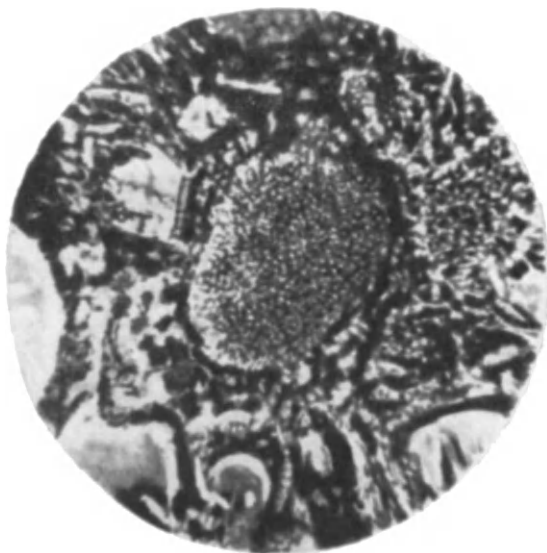


FIG. 32. Xylem vessels and parenchyma filled with bacteria ($\times 960$).



FIG. 33. The humus-like substances in decomposing lucerne root ($\times 270$).

Further observations on the anatomical structure of lucerne roots revealed another curious phenomenon: during the microscopic examination of areas of parenchyma filled with myxobacteria it was possible to observe a gradual lysis of the plasma and its conversion into brown humus-like substances; the latter occurred in the vicinity of the xylem vessels and concealed their walls. One of these root sections, 75 days after the start of the experiment, is shown on the photomicrograph (Fig. 33).



FIG. 34. The xylem vessels after the removal of humus substances ($\times 270$).

These observations, which were consistently repeated in a number of experiments, led us to conclude that the formation of brown humus substances is associated with the decomposition of wood parenchyma by cellulose myxobacteria with the possible participation, also, of libriform tissue in humus formation; at this stage of humification lignified tissues of the xylem vessels were still unaffected by decomposition. We convinced ourselves of the correctness of this by means of a simple procedure: by pressing and washing the humified roots with water we removed the brown substances and then prepared root sections from the residue. The appearance of the lignified walls of the xylem vessels in a section prepared in this way (see Fig. 34) showed that they had still preserved their structure. When treated with phloroglucinol and HCl they gave a distinct reaction for lignin.

These observations from laboratory experiments were confirmed by numerous observations in nature on material collected in the field during the ploughing of a perennial-grass sod.

Clover leaves (Kononova and Bel'chikova, 1946). A microscopic examination of different sections of tissues undergoing humification enabled us to distinguish the following stages of humification:

1. A darkening of the leaves 3–4 days after the start of the experiment; this appears to be brought about by the action of oxidizing enzymes in the tissues and also by the activity of mould fungi which form a weft on the leaf surfaces.



FIG. 35. Section of the epidermis of clover leaf at the start of the experiment ($\times 270$).

2. In the following 7–8 days the development of an enormous number of different bacteria and protozoa is observed in the leaf tissues. The number of bacteria is so great that in some sections the tissues are completely filled with them.

A gradual disappearance (like “dissolving”) of the cell walls of the epidermis, particularly noticeable in young leaves, is observed from a micro-

scopic examination of the leaf surface. At the same time, bacteria, found after isolation to be cellulose myxobacteria, have penetrated into the interior of the epidermal cells.

3. These bacteria, which are at first colourless, later group themselves into slimy masses, become brown in colour and completely fill the cell. After some time, the bacterial mass in the cells undergoes lysis and is converted into a brown liquid which seeps out of the cell.

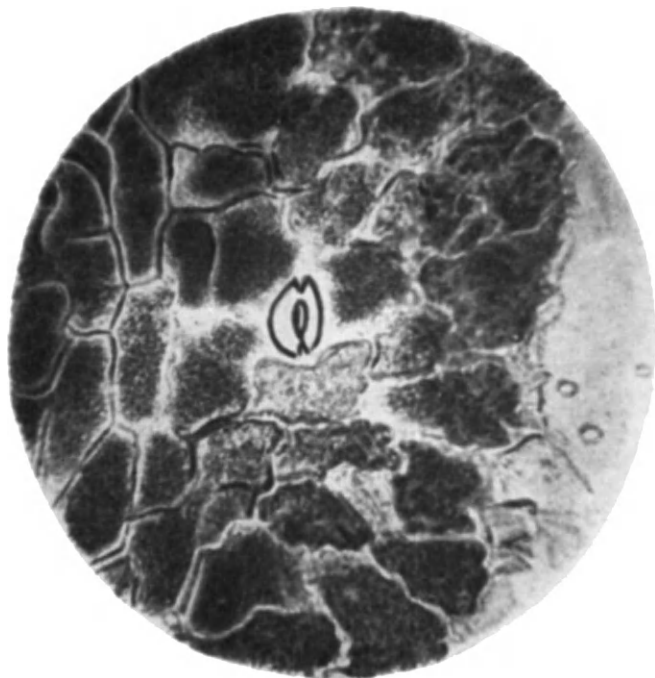


FIG. 36. Epidermal cells of clover leaf filled with bacteria ($\times 720$).

Epidermal cells of clover leaf at the start of the experiment, at a time when they contain a mass of the cellulose myxobacteria and at the time of lysis of the bacterial mass into brown substances, are shown in photomicrographs (Figs. 35, 36, 37).

Under laboratory conditions, the whole process of development of the bacteria and the formation of brown substances takes 7–8 days in clover leaves; 12–15 days after the start of the experiment the entire leaf mass had settled noticeably in the container, being half-submerged in the solution of humus substances.

A microscopic examination of humified clover leaves revealed destroyed mesophyll cells, residues of epidermal cells and little-changed systems of

veins and fibres; the veins were stained a distinct bright-red by treatment with phloroglucinol and HCl. Thus, in this plant material too, the formation of humus substances began before the lignified tissues decomposed.

We also made observations on the decomposition of oak, hazel and birch leaves. Humification proceeded at different rates, being most rapid in hazel leaves, less rapid in oak leaves and slowest in birch leaves; in all cases, however, the formation of humus substances was observed before

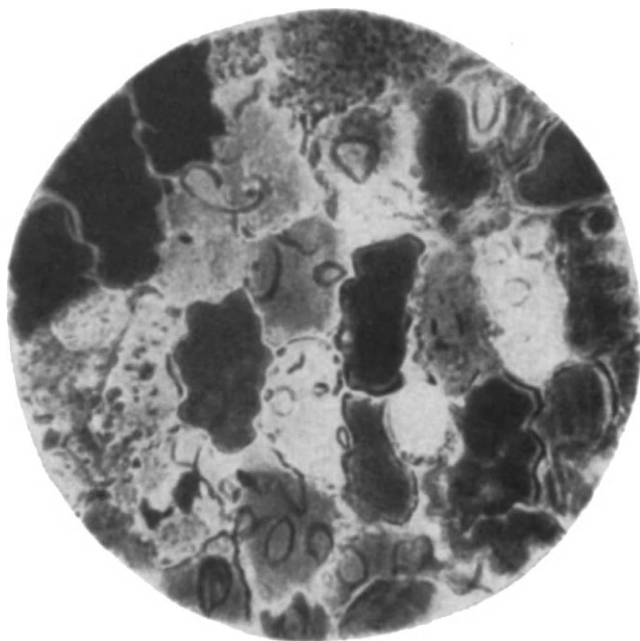


FIG. 37. Epidermal cells of clover leaf at the time of lysis of their contents ($\times 720$).

the decomposition of the lignified tissues occurred (veins of leaf and petiole).

Roots of perennial grasses. In the two previous cases we dealt with the humification of plant residues containing small amounts of lignified tissues, and the latter, because of their position, could not exert a substantial inhibiting effect on the decomposition of more mobile components. As a result of this, the humification of plant residues proceeded rapidly.

Grass roots, on the other hand, serve as an example of a plant residue containing a large amount of lignified tissue, which, because of its close proximity to the more readily decomposed components (Fig. 38), has an inhibiting effect on the decomposition of the roots.

The external layer of the cortex—the exodermis (ex)—consists of cells with strongly suberized walls and the internal layer—the endodermis (end)—forms a ring of strongly lignified cells. Because the cortex possesses this structure, it acts as a barrier preventing the invasion of the interior of the root by micro-organisms.

Internally, the endodermis is in contact with a discontinuous layer of cells—the pericycle (per). Internal to the pericycle are the vascular

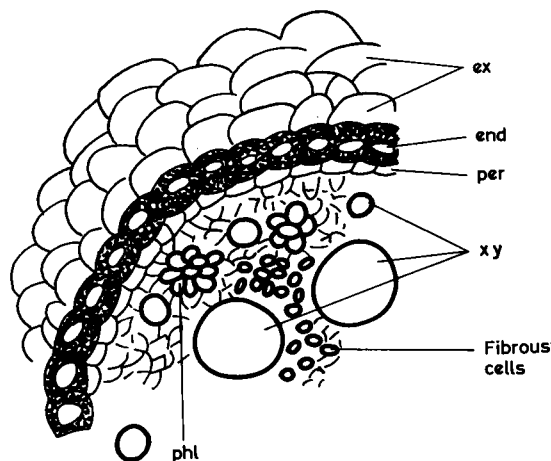


FIG. 38. Structure of the root of *Agropyron tenerum*.

bundles: as a result of the distribution of the root tissue the phloem (phl) and parenchyma (par) are situated close to the xylem vessels and are therefore doubtless affected by the lignified tissues.

As mentioned previously, the roots of perennial grasses are humified slowly; this was also confirmed, by observations on the alteration of their anatomical structure. Only after a few months from the start of the experiment were any changes visible: all the readily decomposable components (pericycle, phloem and parenchyma) disappeared and were replaced by amorphous humus substances. However, cortex, lignified tissues (endodermis) and xylem vessels remained in an unchanged form and continued to stain with phloroglucinol and HCl (Fig. 39).

Observations on the anatomical structure of timothy grass showed a similar pattern of changes: a retarded humification rate, a great stability of the lignified tissues and the formation of humus-like substances at the place of occurrence of phloem and parenchyma of the root.

We shall summarize now the results of our parallel investigations on the chemical composition and anatomical structure of plant residues undergoing humification.

As a result of the systematic examination of the anatomical structure of plant residues during the course of humification it can be regarded as established that during early stages mainly living tissues are decomposed. In clover roots these are the starch-containing medullary rays, the parenchyma and libriform tissue. The suberized layer of the cortex (periderm) and the lignified walls of the xylem vessels show very little change during early humification. In the leaves, the epidermis and parenchyma are

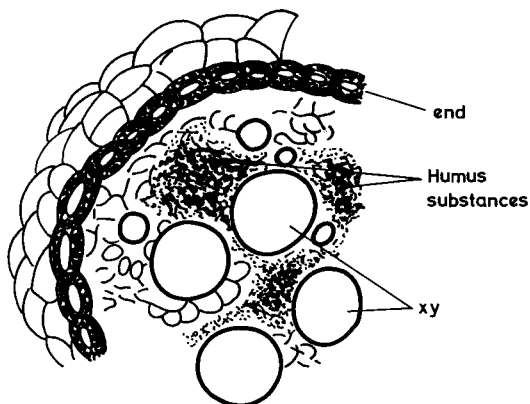


FIG. 39. The humified root of *Agropyron tenerum*.

decomposed rapidly while the lignified tissues—the leaf veins—are preserved. Similarly, in grass roots, the living tissues, namely, the pericycle, the phloem and the parenchyma are decomposed during the early stages of humification whereas the lignified cells (exodermis and endodermis) of the cortex and the xylem vessels are preserved for a long time.

The results of microscopic observations also render data on the group composition of plant residues more intelligible: the complete disappearance of starch together with the medullary rays and the large decrease in the cellulose content due to the intensive decomposition of phloem parenchyma and primary cortex.

Microscopic observations affirm that organic substances can be resynthesized in the form of microbial plasma. It would be expected that the rapid decomposition of tissues containing proteinaceous substances (cambium, pericycle, sieve tubes) would inevitably lead to a decrease in the protein content, and the maceration of the tissues during early humification, to a decrease in hemicelluloses. The fact that there is only a small decrease in these two groups of substances can be attributed, therefore, to their secondary synthesis in the form of microbial plasma. Enormous numbers

of micro-organisms are, in fact, found in decomposing tissues, as has already been pointed out.

Finally, observations on the anatomical structure of humifying plant residues confirm the data of chemical analyses with regard to the resistance of lignified tissues. In our experiments the latter remained undecomposed for a long period.

At the same time, our observations have shown conclusively that the formation of humus substances is also possible at early stages of humification *prior to the decomposition* of lignified tissues and that the new formation of humus substances is associated with the activity of cellulose myxobacteria present in the tissues.

Nature of newly-formed humus substances

The results from the study of humus substances formed at early stages of humification of plant residues are given here.

For the investigations laboratory experiments were carried out using large amounts of leaves and roots of clover (the experimental procedure has been described previously). At the end of the humification process, which lasted 12–15 days with clover leaves and $2-2\frac{1}{2}$ months with clover and lucerne roots, humus substances were isolated from the moist plant residues by squeezing them through muslin. The brown liquid thus obtained was first passed through a linen filter, then through sintered filters Nos. 2, 3 and 4, and finally through a series of membrane filters with pore diameters of $6-0.1\ \mu$. A transparent solution slightly acid in reaction (pH 6.6–6.7) was thus obtained.

By this method, we were able to isolate humus substances in the form of *aqueous solutions near to neutral* in reaction, so that the usual criticisms made when alkali solutions are used—that an alteration of the humus substances occurs during isolation—were no longer valid.

After adding $0.1\ N\ H_2SO_4$ to the filtrate in an amount corresponding to $1/5$ of the total volume, followed by heating on the water-bath at a temperature of $60-70^\circ\ C$, humus substances were precipitated in a brown amorphous form. The filtrate after precipitation was distinctly straw-coloured; it was found that approximately $2/3$ of all the organic substances contained in the original liquid were precipitated by acid and $1/3$ remained in the solution.

The amorphous dark-brown precipitate was washed 2–3 times with distilled water by decantation and then dialysed in small collodion tubes to remove SO_4'' . After dialysis, the precipitate was dried, either on the

water-bath at 60–70° C, or in the air, in which case the gel was spread out in a thin layer on glass.

After drying, the part of the humus substances required for further analysis was subjected to preliminary extraction in the Soxhlet apparatus with a 1:1 ethanol-benzene mixture. In this preparation, the elementary composition (according to Pregl), the methoxyl groups (OCH_3), and also carboxyl (COOH) and hydroxyl (alcoholic and phenolic OH) groups were determined. Comparative data on the elementary composition of humus substances from plant residues and soil humic acids are given in Table 31.

TABLE 31. ELEMENTARY COMPOSITION OF NEWLY-FORMED HUMUS SUBSTANCES AND SOIL HUMIC ACIDS AS PERCENTAGE OF ABSOLUTE DRY ASH-FREE MATERIAL

Materials investigated	C	H	O	N	C : N	C : H	O : H	OCH_3
Humus substances:								
from clover leaves	57.04	5.65	32.35	4.95	11.5	10.1	5.7	2.65
from lucerne roots	53.94	6.46	34.55	5.05	10.7	8.4	5.4	5.80
from clover roots	55.88	5.56	34.63	3.93	14.2	10.0	6.2	4.25
Humic acids:								
from podzolic soil (Dragunov, 1948)	57.94	5.79	31.41	4.86	11.9	10.0	5.4	1.54
from podzolic soil (Natkina, 1940)	56.67	4.79	33.40	5.14	11.0	11.8	7.0	2.26
from chernozem (Shmuk, 1924)	61.84	4.21	30.67	3.28	18.9	14.9	7.3	—
from chernozem (Dragunov, 1948)	57.32	4.25	34.39	4.04	14.2	13.5	8.1	1.17

Newly-formed humus substances and soil humic acids show a similarity in elementary composition. A comparison of the data shows a somewhat lower percentage of carbon and a higher percentage of hydrogen and oxygen, indicating greater hydration in newly-formed humus substances than in soil humic acids. This fact indicates their juvenescence; newly-formed humus substances have a higher percentage of methoxyl than soil humic acids. Dragunov carried out the determination of carboxyl and hydroxyl groups by means of exhaustive methylation with methanol in the presence of HCl , dimethyl sulphate or diazomethane. In addition, he determined the aromatic ring by means of alkali fusion with concentrated KOH .

The results of Dragunov's investigations are given in Table 32 which includes also comparative data for soil humic acids.

TABLE 32. CHEMICAL NATURE OF HUMUS SUBSTANCES OF DIFFERENT ORIGIN AS PERCENTAGE OF DRY ASH-FREE MATERIAL (Dragunov, 1948)

Humic acids	Methoxyl (OCH ₃) linked with the groups:			Products of fusion with KOH
	carboxylic (COOH)	alcoholic (OH)	phenolic (OH)	
From plant residues	8.70	7.56	6.26	pyrocatechol and protocatechuic acid protocatechuic acid trihydroxyphenol (phloroglucinol) of secondary origin
From podzolic soil	8.46	3.37	3.35	
From chernozem soil	9.01	2.11	4.77	

Table 32 shows that newly-formed humus substances have acid characteristics: the number of carboxyl groups present in them was found to be the same as in soil humic acids. Newly-formed humus substances, however, contain alcoholic and phenolic hydroxyl groups (OH) in somewhat larger numbers than soil humic acids.

The products of alkali fusion of humic acids were also found to be of fairly similar nature. In their composition the presence of polyphenols (pyrocatechol and protocatechuic acid) was detected. These compounds were also found in the fusion products of humic acids from podzolic soil.

The presence of the aromatic ring in humic acids of non-lignin origin formed at early stages of humification of plant residues disproves the generally accepted view that the aromatic structure of humic acids is associated with their lignin origin.

CHANGES IN HUMIFIED PLANT RESIDUES ASSOCIATED WITH THE ACTIVITIES OF ANIMALS

In our experiments under laboratory conditions, humified plant residues remained without essential changes for a long time (up to one year and more) being subjected to the slow action of micro-organisms. The residues became densely covered with actinomycetes which apparently utilized not only the most stable components of plant residues but also newly formed humus substances.

However, when the humified plant residues were invaded by small animals they were rapidly ground up and converted into an amorphous humus. This fact is not new. There are a number of works illustrating the great role of various representatives of the fauna in the transformation of plant residues (see Gilyarov, 1939, 1949a, b, 1951, 1953, 1957; Bornebusch, 1930, 1950; Franz, 1943, 1950, 1951; Stoeckli, 1949; and others).

At this point we should mention the well-known observation of Kostychev (1886), who found that humified plant residues (hay, leaves) retained their structure for a long time. However, when small animals, as, for instance, larvae of the midge *Sciara* appeared, the humified material was converted after a very short time into an amorphous mass.

Minute invertebrates, living in the soil and litter, when they pass decomposing plant residues through their alimentary tract, infect them with a bacterial flora and mix them with the soil. Jacot (1936) quotes a number of examples illustrating the enormous amount of work which minute Arthropoda, particularly Collembola and mites, perform in the soil. Minute saprophytic arthropoda living in the soil and in forest litter grind up dead rootlets, rotting leaves, etc.

The nature of humus is linked with the activity of the fauna. Under conditions of excessive moisture and acidity, raw humus — mor — is formed which hinders the activities of animals. On the other hand, in a neutral medium and under moderate moisture conditions these animals digest plant residues intensively, forming "sweet" humus or mull (Müller, 1887; Ramann, 1888; Bornebusch, 1930; Romell, 1935a, b; and others).

Our observations (1944) confirm the great importance of the activity of animals in digesting humified material. In our experiments, humified roots of lucerne and clover retained their structure over several years and the lignified xylem vessels continued to give a distinct reaction for lignin. However, as soon as they were invaded by the midges of *Sciara* and the larvae appeared, the humified material was converted in a few days into an amorphous mass (mull).

During the period of vigorous larval activity it was possible to observe by microscopic examination how the larva grasps plant material, passes it through the alimentary tract and ejects it through the anal aperture. The amazing work of this larva can be judged from the photographs, the first of which shows humified lucerne roots before digestion and the second after their digestion by larvae of the midge *Sciara* (Figs. 40, 41).

An enormous number of insects participate in the mechanical comminution of humified leaves of clover and lucerne. On them we found the



FIG. 40. Humified roots of lucerne before digestion by the larva of *Sciara* ($\times 60$).

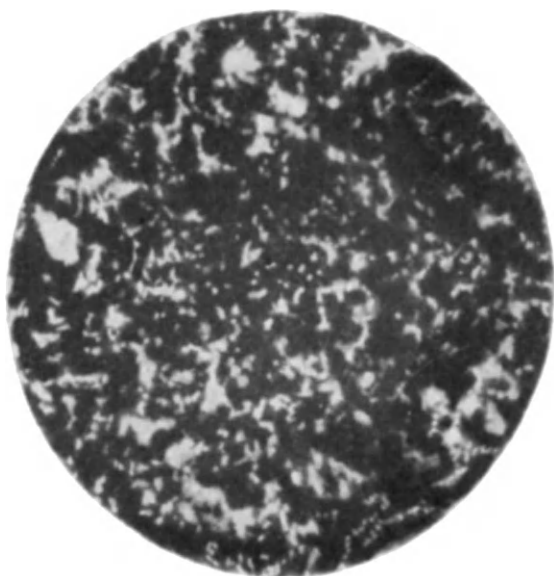


FIG. 41. Humified roots of lucerne after digestion by the larva of *Sciara* ($\times 60$).

larva of *Scatopse fuscipes*, which has mouth parts in the form of a rasp thus adapting it for the grinding of food.

In addition, there are present in humified material a great number of tyroglyphoid mites. By microscopic examination it was possible to observe the work of the mite: in its gullet, which functions like a suction pump, plant material is drawn in, enters the oesophagus, and after digestion is expelled in the form of a finely ground mass (Figs. 42, 43, 44).



FIG. 42. A larva of the midge *Sciara* (mull former) ($\times 60$).

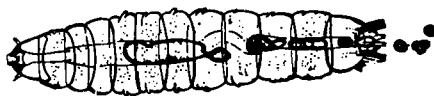


FIG. 43. A larva of *Scatopse fuscipes* ($\times 60$).

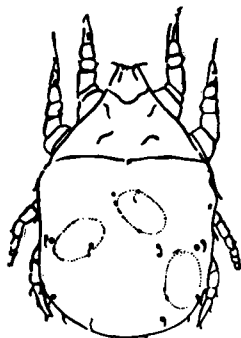


FIG. 44. A tyroglyphoid mite.

Is the role of these organisms limited only to the mechanical comminution of plant material? It is probable that in their alimentary tract plant material is subjected to the digestive action of tissue enzymes and intestinal microflora and therefore becomes more accessible for the further action of numerous representatives of the soil population.

Such phenomena were observed by Sinitsa (1941) in experiments on the digestion of cellulose by the larvae of *Chironomus*; the cellulose which passed through the intestines of these larvae was more readily decomposed by cellulose bacteria. It is not excluded that a similar phenomena may take place with respect to lignin.

There are indications (Tracey, 1951; Deschamps, 1953; Dunger, 1958; Mamaev and Sokolov, 1960) that soil animals are capable of digesting certain simple organic substances (monosaccharides, starch, proteins). Of importance also is the processing by enzymes and the enrichment with microflora of organic residues in the intestines of animals, thus increasing the capacity of complex components of the tissues (cellulose, chitin, lignin) for further transformations.

Not without foundation is the view of some investigators that humus substances can be formed in the intestines of animals through a reaction between products of lignin decomposition and nitrogen-containing organic compounds which are present in the plant residues ingested by animals. The process is brought about with the participation of oxidizing enzymes produced by the intestines (Mason, 1955; Braesch, 1954; Whitehead *et al.*, 1960).

The extent of the activity of insects in the soil can be judged from the following example: in deciduous forest well provided with plant material the number of Collembola is 100,000 per m²; these insects in the course of one year form up to 180 m³ of fine-grained humus per hectare. The extent of this work is probably higher due to the activity of other groups of insects.

This active participation of animals in the transformation of organic residues has led investigators to recognize the enormous role of representatives of the animal kingdom in the formation of soil humus, particularly in forest soils (Kubiena, 1938; Laatsch, 1948; Wittich, 1952).

A great part in the maturing of farmyard manure and in the preparation of various composts, particularly those from municipal wastes, is played by invertebrates (Sauerlandt, 1954a, b); the mechanical comminution of coarse organic residues and their transformation into a loose friable mass takes place with the active participation of animals.

However, their participation in the transformation of organic residues is only one aspect of the diverse role of animals in the soil. Ever since Darwin (1882) established the role of earthworms in the formation of the productive soil layer, the enormous amount of work accomplished by the soil fauna has been well known: this includes the loosening of the soil, its digestion in the alimentary tract and its translocation within the soil profile, the redistribution of reserves of salts, the formation of soil structure, etc. There are also interesting examples of the activity of termites, ants, earthworms, wood-lice, field mice and other animals to be found in the works of Vysotskiĭ (1889), Dima (1903, 1916, 1938, 1941, 1945), Neustruev and Nikitin (1926), Pankov (1921) and, later, Krupenikov (1943, 1951), and other Russian soil scientists.

Interesting investigations on the problem of the formation of water-stable aggregates in the intestines of invertebrates (Collembola, earthworms, etc.) were carried out by Sent-Iler (1938), Ponomareva (1948, 1950, 1953), Zrazhevskii (1957), Finck (1952). It was shown that calcite can be formed in the intestines of earthworms (Meyer, 1943; Ponomareva, 1948).

Soil is the habitat of numerous protozoa, including rhizopoda, flagellates and infusoria. Russell and Hutchinson (1903, 1913) were the first to suggest that protozoa play an active role in the life of the soil. Dogel (1921, 1927), Russell (1923), Brodskii (1930, 1938), Nikolyuk (1957), Gel'tser (1962) and others have established that large numbers of protozoa are present in the soil, that they have antagonistic relationship to bacteria, and that their distribution is closely dependent upon soil conditions.

Protozoa accumulate near organic residues, undoubtedly indicating that they take part in the transformation of these residues. This is favoured by the presence of enzymes in protozoa; for instance, Tracey (1955) found cellulose and chitinase in soil amoeba.

By direct observation on soil populations using capillary microscopy, Aristovskaya (1956, 1961) and Aristovskaya and Parinkina (1961) have shown that this population includes a great number of invertebrates and protozoa (amoeba, nematodes, mites, etc.), whose complex interrelationship with micro-organisms undoubtably affects the processes brought about by the latter.

CONCLUSIONS

A review of works dealing with the study of one of the most important aspects of the problem of soil humus—the biochemistry of humus formation—makes it possible for us to reconsider a number of points which have been generally accepted in the past.

The diverse phenomena which, in combination, constitute the process of humus formation are classified in two stages: the decomposition of tissue components to simpler, chemically individual substances → the synthesis of high-molecular-weight substances (humus substances).

At present there can be no doubt that the most important factor in this process is the activity of micro-organisms. Not only does the first stage—the decomposition of the original plant residues—depend on it, but also, through the participation of oxidizing enzymes of microbes which serve as biocatalysts, it accelerates the second stage—the synthesis of humus substances.

There is also no doubt that all the original substances are subjected to great changes during humification. These include the biochemical conversion of open-chain compounds into aromatic compounds (for instance, the fermentation of carbohydrates with the formation of polyphenols), which may subsequently become components in the formation of humic acids.

Moreover, it is possible for aromatic substances to be split by micro-organisms into open-chain compounds and even into products of complete mineralization when their participation in humus formation is excluded. Finally, the participation of different plant substances in the new formation of humus substances can be brought about through the plasma of micro-organisms, the decomposition products of which can also serve as components for the formation of humus substances.

In accordance with this, the previous classification of plant substances into two groups: direct (e.g. lignin) and indirect (e.g. cellulose) sources of humus substances finds no confirmation in present-day works. Since plant materials are subjected to such complex changes during the humification process they all, in our opinion, serve as indirect sources of humus substances.

For a further study of this complicated section of the soil-humus problem—the biochemistry of humus formation—it will be necessary to overcome many difficulties with regard to method. In our opinion, there should be a more detailed study of the changes of the plant organism as a whole, closely linking this cycle of investigations with investigations on the biochemistry of the process and on the micro-organisms participating in it, studying, at the same time, the nature and properties of the newly formed humus substances.

CHAPTER 4

THE IMPORTANCE OF ORGANIC MATTER IN SOIL FORMATION AND SOIL FERTILITY

IN CONSIDERING the important effects of organic matter on soil phenomena, it should first be mentioned that soil formation is closely linked with the action of diverse forms of organic substances on the parent rock and that we are dealing here with a "bio-geochemical" process. The pioneers in this process are apparently micro-organisms, whose participation in the natural circulation of iron, sulphur, calcium, silica, phosphorus and other elements was shown by many investigators (Vinogradskiĭ, 1896; Nadson, 1903; Omelyanskiĭ, 1927; and others).

The importance of organic matter in the soil is implicit in the definition of soil, which recognizes fertility as the unique and constant feature distinguishing soil from the parent rock. According to Williams, soil fertility is the simultaneous and complete provision of all the plant requirements in water and nutrients.

In the formation of a fertile soil, organic substances play a direct part as they are the sources of plant nutrients which are liberated in available forms during mineralization. But organic substances also play an indirect part. The supplies of nutrients and water for the plant are most readily provided in soil of good structure; in building soil of good structure organic substances represent the most important factor.

Besides being a source of nutrients for the plant, and the most important factor in structure formation, organic matter has also a fundamental effect on the physical properties of the soil (water-holding capacity, heat regime) and determines to a large degree such physico-chemical properties as the exchange capacity and buffering properties; these properties are of great importance not only in controlling the uptake of nutrients by the plant and their retention in the soil but also in suppressing the deleterious effect of soil acidity, etc. In addition, soil organic matter has a direct effect on the plant. There is, in fact, evidence that small amounts of certain organic substances occurring in soil (e.g. benzoic acid, vanillin) are toxic to the plant. At the same time, there is conclusive evidence that quite

small amounts of certain organic substances (highly dispersed humic acids, some aromatic compounds, and organic acids—products of the deamination of amino acids) have a definite, positive effect on the growth and development of the plant. This fact itself is of very great interest.

In the following review, the most important aspects showing the role of organic matter in soil phenomena are summarized.

THE ROLE OF ORGANIC MATTER IN THE WEATHERING AND DECOMPOSITION OF SOIL MINERALS

The simplest form of the action of organic substances on the mineral part of the soil is the dissolving of phosphates, calcium and magnesium carbonates and other compounds by root exudates (CO_2 and organic acids) and by various products of microbial activity. Among the latter are mineral compounds (CO_2 , HNO_2 , HNO_3 , H_2S , etc.) and organic acids of low molecular weight (butyric, lactic, acetic, propionic, gluconic, oxalic, fumaric, etc.).

Omelyanskii (1927) provided some excellent examples of the dissolving of inorganic compounds in products of microbial activity: the dissolving of MgCO_3 and Mg ammonium phosphate in selective media occupied by nitrifying organisms; the dissolving of chalk in lactic acid produced by lactic-acid bacteria and in butyric acid formed by anaerobic butyric-acid bacteria; the dissolving of calcium phosphate in the metabolic products of *Bac. megatherium*.

Ravich-Shcherbo (1928) observed the dissolving of mineral carbonates—calcite (CaCO_3), aragonite, magnesite (MgCO_3), dolomite, siderite (FeCO_3)—in the presence of metabolic products of lactic-acid bacteria, butyric-acid bacteria, nitrifying bacteria and anaerobic nitrogen-fixers.

All these phenomena are undoubtedly of very great importance in the soil because they are responsible for bringing about the conversion of a number of chemical elements into forms available to plants. Of the older works on the conversion of phosphates into available forms, I shall only refer to that of Stoklasa (1911); among more recent works are those of Pikovskaya (1948), Gerretsen (1948), Muromtsev (1955, 1957), Nikitin (1959), Berezova (1960), Myśków (1960) and Sperber (1958). Aleksandrov (1949) isolated bacteria capable of decomposing potassium aluminosilicate with the production of available potassium.

Webley *et al.* (1960) showed that an unidentified species of *Pseudomonas* isolated from the soil decomposed natural and synthetic silicates forming chelates, and also dissolved phosphates.

In Table 33 data are given illustrating the greater solubility of phosphates and phosphoric-acid fertilizers in acids of low molecular weight compared with water containing carbon dioxide.

TABLE 33. SOLUBILITY OF VARIOUS PHOSPHATES IN ORGANIC ACIDS (Waksman, 1927)

Phosphates	P ₂ O ₅ (%)	Amount dissolved in 0.5% acid as % of total content		Amount dissolved in water contain- ing CO ₂ as % of total content
		acetic	fumaric	
Dicalcium phosphate	41.0	97.13	99.54	45.79
Tricalcium phosphate	41.0	73.83	90.90	25.01
Monodiferric phosphate	47.0	19.58	29.35	27.41
Triferric phosphate	38.0	8.13	16.00	7.87
Triammonium phosphate	44.0	22.09	93.79	—
"Florida" phosphate	36.0	16.31	54.04	—
Granitic soil	0.103	7.76	6.79	4.85
Basaltic soil	0.180	7.22	8.33	5.50

The conversion of difficultly soluble phosphates into forms easily available to plants by the influence of products of bacterial activity has been reported in numerous works. On this basis, Kreybig (1953) developed a method for the production of "biophosphates" (which form an effective fertilizer) from phosphates and apatites.

Besides dissolving minerals micro-organisms can, as a secondary result of their activity, also decompose various types of minerals and rocks.

Vernadskiĭ (1927) showed that under the complex biochemical conditions existing between organisms and water containing oxygen, carbon dioxide and organic substances there occurs: a decomposition of silicates and aluminosilicates, an isolation of hydrated ferric oxide from compounds rich in ferrous oxide, the formation of alkali and alkaline-earth carbonates which are mostly soluble in water, the precipitation of colloids (or sols) of silica, kaolin, clays and other aluminosilicic acids and the destruction of the link of silica and alumina with metals.

Vinogradov (1949), in his teaching about biogeochemical provinces, developed the hypothesis of the association of living organisms with the surrounding medium, which is very important in the biogeochemistry of a number of elements (Al, Na, Ca, S, Cl, etc.). Polnov (1945, 1947, 1948) developed the idea that living matter plays a leading role in the geochemistry of the upper part of the earth's crust. During his observations on the weathering of rocks, he found that this process is associated with the

activity of lithophilic organisms which were able to colonize and alter the rock before it became a marl deposit.

Polynov's theory about the weathering action of lithophilic vegetation (lichens, mosses, algae, micro-organisms) during the early stage of soil formation in the hilly and high mountain regions of the Caucasus and Tyan'-Shan' is being developed by Assing (1949), Aidinyan (1949), Yari-lova (1950, 1956), Glazovskaya (1950, 1952), Bobritskaya (1950), Parfe-nova (1950), and Parfenova and Yari-lova (1956). It has also been found that even under the severe climatic conditions of the Antarctic, the weathering and primary soil formation are brought about with the help of various groups of organisms (Glazovskaya, 1958). Microbiological investigations of the rocks of the Caucasus (Krasil'nikov, 1949; Aleksandrova, 1953a), Tyan'-Shan' (Novogrudskii, 1950; Tauson, 1948), and Khibin (Roizin, 1960) have established that blue-green and green algae, fungi and actinomycetes play an active part in weathering.

The biochemistry of these processes is still not clear. Apparently, in some cases, micro-organisms during the decomposition of stable compounds are able to utilize the essential nutrient elements which they contain. Vernadskii showed that minerals possessing the kaolin nucleus may be used by micro-organisms as a source of energy, for as its structure indicates the kaolin nucleus represents an endothermic compound and its decomposition is accompanied by the production of heat. He states, "If this is true, then the life of those organisms is supported in the long run, not by solar energy, but by atomic energy—by the energy of radioactive fission bringing about the fusion of magma" (1927, p. 141).

The corrosion of rocks as a result of the activity of various bacteria and algae was observed by many investigators (Jensen, Ru, Müntz and others, see Waksman, 1927). Bassalick (1912) in experiments with selective bacterial cultures observed the decomposition of feldspars with the formation of soluble forms of K_2O and SiO_2 which could be detected in the nutrient medium. At the same time, the bacteria showing the greatest activity were those which produced organic acids during growth (e.g. *Bac. amylobacter*). In some cases, the decomposition of minerals occurred during their direct contact with the bacterial plasma; in an experiment with *Bac. extroquens*, which fermented organic substances to CO_2 and H_2O , an appreciable decomposition of feldspar was observed in cases where micro-organisms formed a continuous film on the mineral particles; the first compounds to pass into the nutrient solution were alkali compounds, then came alkaline-earth and iron-containing compounds; the most resistant were silicic acid and aluminium oxide.

Novorossova, Remezov and Sushkina (1947) demonstrated the decomposition of kaolin and feldspar with the formation of soluble forms of SiO_2 and Al_2O_3 produced by the activity of a mixed microflora. The experiments were carried out in a nutrient medium containing glucose and organic nitrogen. The decomposition of silicates by products of the activity of many fungi and bacteria has been established by Webley, Duff and Mitchell (1960), Duff, Webley and Scott (1963) and Henderson and Duff (1963).

Algae as well as bacteria produce a considerable decomposition of minerals. Many investigators observed the growth of algae on mountain summits and rocks and noticed their decomposing action at the site of the colony (Tauson, 1948). Merrey and Irwin (1891, see Waksman, 1927) in investigating the silica of oceans encountered the decomposition of clays by diatoms. Vernadskii (1922) showed experimentally that where diatoms are present in a mixed culture with bacteria, the decomposition of kaolin clay occurs. This was later confirmed by Vinogradov and Boïchenko (1942), who found that the diatoms *Navicula minuscula* and *Nitschia palla* promoted the weathering of nacrite; this begins with the contact of the pectinaceous algal slime with the mineral crystals, and is accompanied by the appearance of soluble aluminium in the medium. It is possible that in the case of diatoms, the decomposition of kaolin is explained by the increased requirement of these organisms for silica which is necessary for the formation of their shells.

Considerable decomposition is brought about under natural conditions by lichens. Bachmann (1904, 1907, 1911) observed the decomposition of granite by encrusting lichens, mica being most markedly affected. Of interest also are Bachmann's observations on the decomposition of garnet (almandine) in micaceous shale by the lichen *Rhizocarpon geographicum* with the formation of amorphous iron compounds. Yarilova (1947), by examining microscopic sections, was able to demonstrate the role of lichens in the weathering of massive crystalline rocks and their mineral constituents.

Investigators usually attribute the decomposing action of lichens on a substrate to the increased concentrations of carbon dioxide and oxygen in the medium, acting as weak reagents. Yet it is known that such compounds as garnet and quartz are decomposed only by very strong reagents (hydrofluoric acid). A somewhat different explanation of the decomposing action of lichens on minerals was given by Fry (1924). In his opinion, the effect was due to the direct action of the slimy body of the lichen on the substratum—during desiccation, slime tears away particles (lamellae)

from the rock and mineral just as a layer of gelatin applied to glass contracts during desiccation, breaking off and carrying away particles of glass. This explanation undoubtedly has some foundation, as it is well known that the slime of micro-organisms has a very great adhesive action, and that the separation of cohering particles by desiccation of the slime is only possible with the application of considerable force (see the works of Shrikhande, 1933).

Mechanical disintegration, in this case also, is accompanied by chemical changes due to the action on the rock of products of lichen activity. Levin (1949), from an investigation of the role of lichens in the weathering of limestone and diorite, concluded that lichens cause mechanical disintegration by penetrating the rock and tearing away lamellar-shaped particles from the surfaces of minerals. In addition, lichens promote the chemical weathering of rock-forming minerals; the biochemical action on the minerals is important as it is accompanied by a destruction of the link between constituent elements of the mineral, such as that occurring between Si and Al in aluminosilicates, with the subsequent absorption of these elements by lichens.

These examples from the literature indicate that the decomposition of mineral constituents of the soil may involve the participation of organic substances of non-specific nature—acids of low molecular weight and other organic compounds among which are the exudates of the roots of higher plants or products of microbial activity.

During recent years, data indicating the mechanism of the action of micro-organisms and the metabolic products of their activity on minerals have been obtained by various investigators. Organic substances possessing chelating properties have been found to have a pronounced effect on the chemistry of minerals.

This group of substances includes many compounds of an individual nature occurring widely in the soil: organic acids (in particular, lichenic acids), derivatives of polyphenols, uronic acids and certain pigments, amino-sugars, etc. Some of them are decomposition products of organic residues, although, in the main, they are products of the activity of lichens, fungi, bacteria and other groups of micro-organisms; there are also the constituents of the root exudates of higher plants. An important part in these processes is played by melanoidins.

These substances, during contact with rocks and minerals, appear to extract aluminium, iron, manganese, copper and certain other elements from them with the formation of complex and intra-complex compounds (chelates). Owing to their ability to change into soluble forms over a wide

range of pH of the medium, these compounds possess high mobility and participate actively, not only during the initial stages, but also at later stages of soil formation. In particular, complex and intra-complex compounds of a wide range of organic substances play an important part in the podzol-forming process and in the supply of trace elements (copper, manganese, zinc, cobalt, etc.) to plants.

There is an extensive literature on this subject; its survey and review are given in the books of Kovda and co-workers (1959) and of Peive (1961), and in a number of papers (see: *Soil Sci.* Vol. 84 (2), 1951; Schatz, 1954, 1955; Scheffer, Ulrich and Hiestermann, 1957; Scholz, 1957; De Kock, 1955, 1960; Antipov-Karataev and Tsyurupa, 1961; D'yakonova, 1962; and others).

Complex and intra-complex compounds are very important in the geochemistry of the elements Fe, Al, Cu, U, As, Zn, Se, V, Ge, Mn and others.

Phenols having OH or COOH and OH groups in the ortho-position (Halmekoski, 1959; Shnaiderman, 1959, 1960; Drozdova, Kravtsova and Tobelko, 1961; Manskaya and Kodina, 1963), flavanoid-type substances (Kanno, 1960) and melanoidins (Manskaya, Drozdova and Emel'yanova, 1958) all have a tendency to form such metallo-organic compounds.

Not less important is the role played by strictly humus substances in the geochemistry of the elements Au, Mo, Re, Fe, Cu, etc. (Zvyaginsev, 1941; Shcherbina, 1956; Drozdova and Emel'yanova, 1960; Manskaya, Drozdova and Emel'yanova, 1956; Pospisil, 1962; Kuznetsova and Saukov, 1961; Chuveleva, Chmutov and Nazarov, 1962).

It should be mentioned here that, as Sprengel pointed out long ago, humic acids may decompose silicates, forming silicic acid; Berzelius showed that crenic and apocrenic acids destroy silicates. Many workers (Zenft, Tarkhov, Karster, Rodzyanko, Meshcherskii, and others—see Glinka, 1935, and also Smirnov, 1915; Graham, 1941; Ponomareva, 1950, 1951; Marel, 1949) have demonstrated experimentally that solutions of humic, crenic and apocrenic acids decompose various minerals (in particular, silicates and alumino-silicates). Utilization of P_2O_5 by plants was increased in the presence of humic acids (Askinazi, 1938; Chaminade, 1946; Wojciechowski—see Niklewski, 1958; Szymanski, 1962; Ginzburg, 1960). The character of this action depends both upon the nature of the humus substances and upon the nature of the minerals.

The most active role in the decomposition of rocks is played by fulvic acids and apparently also by members of the humic acid group related to them, which, as we shall see below, possess chelating properties. The

experiments of Marel (1949) indicated that some minerals were more resistant than others to decomposition by humic and low-molecular-weight acids. Amphiboles were most easily decomposed, muscovite and epidote less easily, zircon was more difficult to decompose and tourmaline and quartz were very resistant.

THE ROLE OF ORGANIC MATTER IN THE FORMATION OF SOIL PROFILES; FORMS OF LINKAGE BETWEEN SOIL ORGANIC MATTER AND THE MINERAL PART OF THE SOIL

The heterogeneity of a soil profile results from the alteration of the parent material and the redistribution of materials during the soil-forming process. In this process, soil organic matter plays an important role.

Only a small part of the organic matter is present in the soil in a free state; the major portion is linked with the mineral part of the soil. The nature of the metallo-organic compounds (called, in soil science, organo-mineral compounds) which is different for different soils, is at present not yet fully clear.

Tyurin (1937), Springer (1936) and Tyulin (1938) have classified the possible forms of link between humus substances and the mineral part of the soil. Tyurin has outlined the following possible forms of link (the terminology is that given in his monograph):

1. Humus substances occurring in a free or almost free state.
2. Humus substances in the form of strong base humates; humates of (a) Ca and in part Mg; (b) Na (and Mg).
3. Humus substances in the form of humates and gels mixed with aluminium and iron hydroxides.
4. Humus substances firmly linked with clay ("clay-humus").
5. Humus substances in the form of complex organo-mineral compounds (with Al, Fe, P, S).

In recent years, attempts have been made to define more exactly the forms of link between humus substances and the mineral part of the soil in relation to various soils, and to explain their mode of formation (Antipov-Karataev, Kellerman and Khan, 1948; Khan, 1946, 1950; Beutelspacher, 1955; Aleksandrova, 1954, 1960a, b, 1962; Aleksandrova and Nad', 1958; Broadbent *et al.*, 1952, 1957, 1961; Harada, 1957; Scheffer and Ulrich, 1960; Deuel, 1960; Stobbe and Wright, 1959; Duchaufour, 1963).

According to Antipov-Karataev, the classification of metallo-organic compounds may be represented as follows:

1. Salts of low-molecular-weight organic acids (acetates, oxalates, etc.).
2. Salts of humic and fulvic acids (humates, fulvates).
3. Complex and intra-complex compounds (chelates).
4. Adsorption organo-mineral compounds ("argillites"), which include compounds of fulvic and humic acids with hydrated sesquioxides and adsorption compounds with clay particles.

1. *Salts of low-molecular-weight organic acids* are formed when the acids (acetic, oxalic, lactic, fumaric, and others primarily the products of microbial and animal activity) react with minerals (calcite, magnesite, siderite, etc.—see the previous section of this chapter) and with salts (sodium, potassium, calcium, phosphorus, etc.) of mineral acids. A certain amount of some salts of low-molecular-weight organic acids, in particular oxalates, may enter the soil with plant residues.

2. *Salts of humic and fulvic acids with cations of alkali and alkaline earth metals*—humates and fulvates of Ca, Mg, K, Na, Al, Fe, NH_4 , which are characteristic of the soil. Conductimetric and potentiometric titrations of humic and fulvic acid solutions show that exchange reactions occur with soluble alkaline or neutral salts of alkali or alkaline earth bases (Stadnikov and co-workers, 1934; Antipov-Karataev and co-workers, 1935, 1947; Aleksandrova, 1954, 1962). The hydrogen of functional groups—carboxyl and phenolic hydroxyls—is replaced successively by a metal, the replacement increasing with the increase of solution pH (Antipov-Karataev and Khainskii, 1935; Rydalevskaya and Tishchenko, 1944). The most complete replacement is observed in strongly alkaline media (pH 10–12); however, exchange reactions with $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ may be accompanied by simultaneous molecular sorption of these hydroxides (Syskov, 1936).

At neutral pH, only the hydrogen of carboxyl groups is replaced by metals. This has recently been demonstrated by Larina and Kasatochkin (1957), who used infra-red spectroscopy to study the reaction between humic acids and calcium and barium salts, and by Orlov and Nesterenko (1960) for similar reactions with salts of copper, nickel, zinc and cobalt. Investigating the products formed by humic acids and the above-mentioned salts, these authors discovered that the band near 5.9μ (1700 cm^{-1}), which is characteristic for carboxyl groups disappears from the spectra. During this reaction the ionized group COO^- is formed.

The replacement of hydrogen in the functional groups of humus substances is influenced both by the pH of the medium and by the concentration of the substance. Orlov and Nesterenko (1960) note that in their experiments the exchange reaction described above occurred with dilute sols and dilute salt solutions. At high sol concentration (2–3 mg per ml) the reaction is complicated by partial coagulation of humic acids.

Salts of humic acids and fulvic acids have different solubilities. Alkali humates form highly dispersed colloidal and molecular solutions, whereas humates of divalent cations are less soluble, Ca-humate in particular being less soluble than Mg-humate.

Ponomereva (1949) has shown that the fulvates of alkali metals are soluble in water at all pH's, but the fulvates of the alkaline earths precipitate at $\text{pH} > 10$; they do not precipitate under acid, neutral or slightly alkaline conditions. Hydrated ferric oxide in its complex with fulvic acid is mobile over a much wider range of conditions than is hydrated aluminium oxide.

In the soil the interaction of humus substances with alkali and alkaline earth bases is complicated by the simultaneous formation of other organo-mineral compounds, mainly alumino-ferro-humus derivatives. So in most cases, compounds more complex than the pure humates and fulvates of K, Na, Mg and Ca are formed in the soil (Aleksandrova, 1960a, b; Harada, 1957).

3. *The group of complex compounds* formed between organic substances and iron, aluminium, manganese, copper and other elements is characteristic of the soil. Both organic compounds of an individual nature and also strictly humus substances may take part in their formation. These compounds may be of two types:

- (1) *Complex* compounds in which each radical is linked by only one co-ordination bond to the central ion;
- (2) *Intra-complex* compounds (chelates) in which a radical of the molecule is linked to the central ion by several co-ordination bonds. In chelates, the ion of a metal forms bonds with a molecule of chelating organic substance which contains two neighbouring groups able to combine with the metal.

Various chelate structures are known, differing in the type of link with the metal. Usually, chelates contain an anion group in which a hydrogen ion can be replaced by a metal ion. The difference between complex and intra-complex compounds is illustrated in Fig. 45 (Scheffer, Ulrich and Hiester mann, 1957).

The concentrations both of the humic and fulvic acids and of the metal ions are extremely important in the formation of complexes, as was shown by Ponomereva (1949), Fat'yanov (1956), Broadbent and Ott (1957) and Martin and Reeve (1960). From studies of the complexes between copper and humic acids, Drozdova (1960) showed by electrophoresis that if the quantity of added copper was large compared with the humic acid, all the humic acid was immobilized, forming an insoluble complex at the point of application. If the quantity of added copper was small, a mobile negatively charged complex was formed.

Equally important is the pH of the medium; Scholz (1957) and Kawaguchi and Kyuma (1959) showed that intra-complex compounds of iron with humus substances and EDTA were stable in acid media. At pH 7.5, the complex begins to take up hydroxyl ions; at an alkaline reaction the complex decomposes forming $\text{Fe}(\text{OH})_3$.

Complex and particularly intra-complex metallo-organic compounds play an active role in weathering during the early stages of soil formation and also in the subsequent stages, such as in the development of the podzol-forming process, which is discussed below.

4. *The group of adsorption organo-mineral compounds* ("argillites") varies in composition and includes not only derivatives of humates and fulvates but also humus substances, linked with clay.

The character of the link between humus substances and clay minerals remains obscure. A number of authors (Antipov-Karataev, Kellerman and Khan, 1948; Khan, 1946, 1950) consider that the complexes between humus substances and clays are probably formed by bridging through the exchangeable cations Ca, Mg and Al, as proposed by Gapon (1937).

In addition these authors consider that, because of great difficulty in isolating humus substances from the humin fraction, they may possibly penetrate into the interlayer space of the crystalline clay mineral lattice. However, Aleksandrova considers such a phenomenon very unlikely, because the molecules of humic acids have a specific form, the diameter of which exceeds the interlayer space in the crystalline lattice of clay minerals.

According to Aleksandrova (1962), stable clay-humus complexes are formed in the soil with the help of sesquioxides, which make specific bridges between humus substances and the crystalline lattice of clay minerals. These bridges are imagined as complex aluminium and iron humus compounds with non-silicate forms of sesquioxides. They are fixed to the surface of the clay minerals during dehydration by a process of adhesion at the expense of intermolecular types of linkage (Aleksandrova and Nad', 1958).

The mechanism whereby humus substances interact with clay minerals has been the subject of work by Mukherjee (1956), Khan (1959), Evans and Russell (1959), Sen (1960), and Kobo and Fujisawa (1963). Sen suggests that during the interaction of clay with humic acids, two types of linkage take place. In the first—unstable—type of linkage, humic acid is arranged on the external micelle surface of the clay; this humic acid is easily extracted by alkali. The second—stable—type of linkage (humic acid is not extracted by alkali) is formed from the interaction of clay, humic acid and the exchangeable cations (Fe^{3+} , Al^{3+} , Ca^{2+} and Mg^{2+}) occurring in the lattice of the clay mineral; the $-\text{OH}$ and $-\text{COOH}$ groups in the humic acid take part in the linkage.

Aleshin and Shaimukhamedov (1962) using differential thermal analysis, concluded that part of the organic substance is situated on the surface of the mineral particles and part sorbed between the layers of the mineral lattice.

The possible interaction between particular types of organic compounds (proteins, amino acids, carbohydrates, etc.) and clay minerals, and the importance of these phenomena for the establishment of soil structure and for fixing organic substances in the soil will be discussed in the appropriate chapters (see the section "The role of organic matter in the formation of soil structure" in Chapter 4, and the section "The influence of chemical and physico-chemical soil properties on humus formation" in Chapter 5).

We shall now attempt, on the basis of the above account, to describe the forms of metallo-organic compounds that are characteristic of different soil types.

Metallo-organic compounds may be present in any soil, although in different relative proportions. It appears that simple salts of low-molecular-weight organic acids occur in the soil in a dispersed state; the concentrations of these salts in any soil or individual soil horizons are not known.

Only very small amounts of the second group of substances (humates and fulvates of alkali and alkaline earth bases) are present in the soil in a pure form; they occur mainly in more complex forms as aluminium and iron derivatives. It is true to say that these complex forms of metallo-organic compounds are characteristic of the chernozem type of soil. Their nature in these soils is determined by the high exchangeable calcium and clay mineral contents, and by the predominance in the humus of humic acids that are easily precipitated by electrolytes.¹

¹ See Chapter 2, page 73, "The structure of the humic acid molecule".

Because of the characteristic absence of a leaching water-regime in chernozem soils, this complex system of organo-mineral colloids is stable and more or less homogeneous within the soil profile.

The profile of podzolic soils is formed in a different way and complex and intra-complex compounds of iron and aluminium play an active role in its formation. As pointed out in the previous section, many organic substances of an individual nature (organic acids, in particular dicarboxylic acids, uronic acids, lichenic acids and also pigments, amino sugars, certain amino acids, etc.) have a tendency to form such metallo-organic compounds.

Vishnyakov and Rabinovich (1935), Rode (1937) and Tyurin (1944) have discussed the possible role of dicarboxylic acids (citric, tartaric, oxalic, and other acids which form complex compounds with iron and aluminium) in podzol formation.

In recent years, the attention of research workers has been turned to the polyphenol group of substances, formed in soil, leaf fall and forest litter during the decomposition of lignins and tannins. Their ability to form intra-complex compounds with iron has been shown by a number of workers (Bloomfield, 1953, 1954, 1957; Lossaint, 1954, 1956, 1957, 1958; Coulson, Davies and Lewis, 1960) who note the essential role of these substances in the translocation of iron and in the development of the podzol forming process.

Deuel (1960) and Hess, Bach and Deuel (1960) have shown that, according to the same principle, the catechols (pyrogallol, gallic acid, pyrocatechol, etc.) decompose such resistant compounds as silicates and aluminosilicates (Si-O-Si and Si-O-Al) forming complexes with silica and aluminium.

Strictly humus substances have the ability to form complex and intra-complex compounds (chelates) with iron, aluminium, copper and other polyvalent ions. This ability is determined to a considerable extent by the presence in their molecules of hydrophilic groups situated in side radicals. The same view is expressed by Kawaguchi and Kyuma (1959). It is for this reason that fulvic acids have the greatest tendency to form intra-complex compounds with a number of cations, notably iron. However, humic acids probably also take part in the formation of complex compounds.

In our investigations (Kononova and Titova, 1961) we used electrophoresis to fractionate fulvic acids that had been purified by electrodiagnosis. When the electrophoretograms were treated with 4% $K_4[Fe(CN)_6]$, negatively-charged iron-humus complexes appeared in the form of characteristic greenish-blue spots. It is interesting that complexes similar in nature

to those of fulvic acids were detected by us in humic acids isolated from the humus-illuvial horizon of a strongly podzolic soil. No less interesting was the study by electrophoresis of complexes obtained artificially when humus substances were saturated with iron. It was shown that humic

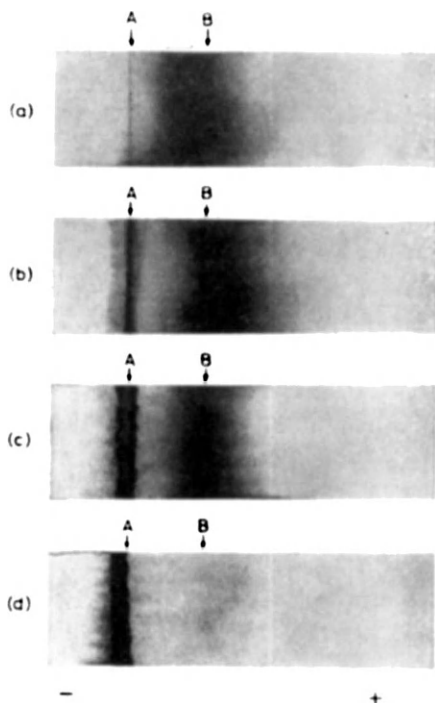


FIG. 46. Electrophoretograms of humus substances treated with an acidified solution of $K_4[Fe(CN)_6]$. (a) fulvic acids from a krasnozem; (b) humic acid from the humus-illuvial horizon of a strongly podzolic soil; (c) humic acid from a sod-podzolic soil saturated with iron; (d) humic acid from a chernozem, saturated with iron. A — start; B — zone of location of negatively charged iron-humus complex.

acids from a sod-podzolic soil form not only immobile complexes, but also negatively-charged mobile complexes of chelate type. Humic acids from a chernozem, however, form only immobile complexes with iron (Fig. 46).

Because many organic compounds can form complex or intra-complex compounds with polyvalent ions such as iron, complexes may be present in any soil, as has been shown by Kaurichev and co-workers (1958, 1960), Aleksandrova (1960a) and Kononova and Titova (1961). After extracting soils once with 0.1 N NaF (pH 7.1) and fractionating the extracts by

electrophoresis, Titova (1962) detected in them iron-humus complexes of a chelate type. The carbon content of complexes from the humus-illuvial horizon of a strongly podzolic soil was 32 per cent of the total soil carbon, from krasnozems and mountain-taiga ferruginous soils 12–20 per cent, and from a chernozem, only 7 per cent.

The formation of chelate-type compounds in krasnozems and podzolic soils is favoured by a high content of fulvic acids, of humic acids similar to them in nature, and of products of incompletely humified organic residues having chelating properties. These substances act on primary minerals or hydroxides so that iron, aluminium and probably silica are changed into molecular intra-complex organo-mineral compounds which are stable and negatively charged. These compounds are leached down the soil profile into zones where their stability is disturbed; here they form a humus-illuvial horizon. Antipov-Karataev and Tsyurupa (1961) call such a mode of forming humus-illuvial horizons *molecular-infiltration*.

Because of the reducing properties of fulvic acids (Beres and Kiraly, 1959) and polyphenols, the reduction $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$, which contributes to iron mobilization, occurs not only under anaerobic but also under aerobic conditions. Accordingly, the view that the podzol-forming process must be strictly associated with anaerobic soil conditions or with a seasonal anaerobic-aerobic regime (Yarkov, 1954) is no longer valid.

Organic substances also play an important role in other processes in which soil material is displaced. Thus organic substances take part in the formation of illuvial horizons by *peptization-infiltration*, which occurs without the accompanying destruction of the clay soil mass (Antipov-Karataev and Tsyurupa, 1961); such an example occurs in sols-lessivés.

There are indications that the infiltration transfer of clay is due to the peptizing action of organic substances, though the mechanism of the process is not yet clear. In this connexion, the work of Duchaufour (1957) merits attention; while making comparative studies of organic matter in podzolic soils and sols-lessivés, Duchaufour concluded that development of the podzol-forming process was favoured when the medium was poor in bases and nitrogen and the rate of humification of plant material was low. The products of incomplete humification (in particular, polyphenols) migrate down the soil profile, enriched in iron and aluminium at the expense of the mineral horizons. In sols-lessivés containing adequate exchangeable bases and nitrogen, plant residues are completely humified, with the formation of humic acids. According to Duchaufour, humic acids do not cause much loss of iron. Studying various forms of sols-lessivés Kundler (1961) has found that the brown forms differ from the

typical forms (sol-lessivés) in having a higher humic acid content of the humus.

Antipov-Karataev and Tsyurupa (1961) also distinguish a *colloidal-infiltration* mechanism in the formation of illuvial horizons in soils (for instance, in solonetses) in which substances migrate as colloidal dispersions. For such a migration to occur, the soil materials must be decomposed into negatively-charged components. Undoubtedly this way of forming an illuvial horizon in solonetses takes place with the help of humus substances, which, in the presence of exchangeable sodium, are converted into mobile humates. However, the mechanism of this phenomenon is not yet known.

THE ROLE OF ORGANIC MATTER IN THE FORMATION OF SOIL STRUCTURE

The structure of soil is of very great importance in determining its fertility, organic matter being without doubt the most important factor in the formation of soil of good structure. This fact was observed by a number of investigators of the last century (Schloesing, Kostýchev, Wollny) and was developed further by Williams. He worked out such fundamental problems as the importance of structure for soil fertility, the mechanism of structure formation, the role of organic substances in this process and practical measures for the formation of soil of good structure.

Soil with good structure provides the best conditions for supplying water and nutrients to the plant. This agronomically valuable structure should be distinguished, however, from the type of structure which although water-stable, is agronomically deleterious because of its reduced porosity. This condition is observed in the water-stable structure of solonetses, in the B₂ horizon of podzolic soils and in the structure produced by compression in excessively moist soil. This was pointed out by Tyulin and Sklyar (1933), Savvinov (1935), Kachinskiĭ (1947, 1949). With this type of structure, the plant is insufficiently provided with nutrients and air because of the occurrence of reducing conditions.

The best water and nutrient regimes are produced in soil with a fine-crumb macrostructure in which the aggregate size is 1–3 mm. This type of structure is formed under a cover of perennial grass-legume vegetation. The prerequisites which Williams believed to be necessary for the formation of soil of good structure are: (1) the consolidation of the soil particles under pressure from the highly branched root systems of grasses; (2) the formation of active humus of the ulmic- and humic-acid type; (3) the

penetration into the soil crumbs of the highly dispersed (according to Williams, molecular) solutions of ulmic and humic acids; (4) the conversion of these acids into the state of a cement mainly by means of calcium supplied by the roots of legumes from the lower to the upper horizons.

This conversion of humus substances into the state of a cement is irreversible, and therefore after the mechanical dispersion of soil they represent diverse thin films whose conversion into a state in which they could once again cement the soil crumbs requires a long period and certain specific conditions. Therefore, for maintaining the soil in good structure, the provision of newly formed humus substances is essential; this is brought about by the periodic introduction of perennial grasses into the crop rotation.

Williams's ideas on the role of the biological factor in the formation of soil of good structure were developed in the works of other authors. Savvinov (1935), in determining the structure of virgin soils, showed that chernozems under perennial meadow vegetation had the highest degree of water stability, the amount of water-stable aggregates being 80–90 per cent. The curve of soil structure gradually falls in the direction of forest steppe (60–80 per cent) and further towards sod-podzolic soils (30–40 per cent), i.e. in the direction of soils on which grass is replaced by woody vegetation. A sharp fall in the curve of soil structure is also observed on passing towards southern chernozems, then towards chestnut soils (up to 20 per cent) and finally towards serozems (up to 5–10 per cent), i.e. towards soils in which aerobic processes predominate.

The investigations of many authors are devoted to an elucidation of the role of micro-organisms in the formation of a water-stable soil structure. We shall examine the works of some of them. It was shown that water-stable aggregates could be formed through the action of mould fungi, which appear in abundance on fresh plant residues. Mycelia of mould fungi by enmeshing soil particles prevent their dispersion by water; this accounts for the usually observed increase in the number of water-stable aggregates in soil containing plant residues at early stages of humification (e.g. after the ploughing-in of the grass sod and green manures, or after the application of organic manures). This phenomenon is only temporary, however, and comes to an end with the disappearance of the fungal microflora. Only when the mycelium of mould fungi is converted into more stable humification products are the aggregates preserved for a longer period (Kanivets *et al.*, 1938, 1942; Mishustin *et al.*, 1942, 1945; Martin, 1945; Downs, McCalla and Haskins, 1955; Thornton, Cowie and McDonald, 1956).

A positive effect on the creation of water-stable aggregates is produced by bacterial slimes. Gel'tser (1943), who isolated a number of rhizosphere bacteria of the *Pseudomonas* type from the root systems of meadow grasses, demonstrated their capacity for cementing soil particles.

The formation of a water-stable soil structure through the action of bacterial slime was observed by several investigators (McCalla, 1945; Martin, 1945; Peele, 1940; Geoghegan and Brian, 1948; Rennie, Truog and Allen, 1954; Rudakov, 1953; Mehta, Streuli, Müller and Deuel, 1960; Greenland *et al.*, 1961; Clapp, Davis *et al.*, 1962; Salomon, 1963), who showed that slime-forming micro-organisms increased the resistance of the soil to erosion. Nevertheless, it is not only polyuronides of slime that form good structure (Kullman and Koepke, 1961; Deuel, 1960). A positive effect on the formation of a water-stable structure was also observed by Mishustin (1945) when pulverized soil was wetted with bacterial slime. However, he regarded the structure produced by the elements of microbial plasma as unstable and not therefore as valuable as the stable structure produced by humus substances.

In recognizing the formation of soil structure as a dynamic process, Mishustin (1945) held the view that in this process aggregates of unstable and of stable character can be formed. The unstable part of the soil structure can become stable depending on climatic conditions and also on the physicochemical properties of the soil and its state of biogenesis. Mishustin thought that it was theoretically possible for soils with a predominant structure of the first or second type to occur. For instance, in soils poor in colloids and situated in a hot climate an unstable structure predominates (serozems), while in the northern zones (chernozems) the stable structure produced by humus substances is more typical.

Soil aggregates formed in the alimentary canal of animals (particularly earthworms), where the soil particles are cemented by their slimy secretions, possess a very high stability (see Chapter 3 on the role of animals in the digestion of plant residues).

However, on the problem of the interaction between organic matter and mineral substances during the formation of aggregates, much is still obscure. Gedroits (1926, see 1955), who studied the mechanism of this process, concluded that two factors are involved: the pressure of the root systems of plants on the soil, and the coagulation of the soil colloids under the influence of calcium ions. The primary micro-aggregates which are formed at the same time are cemented to one another by highly dispersed organic substances of the colloidal complex and so macro-structural aggregates are formed.

Important studies on the mechanism of structure formation in the soil were carried out by Sokolovskii (1921, 1923). He concluded that one of the most agronomically important factors determining the stability of structure and the value of the exchange capacity of the soil is the "active-silt" fraction (which includes active humus), which can be isolated from the soil by saturation with sodium and subsequent peptization with water. The remaining part, which Sokolovskii named "passive silt", participates less actively in soil processes and in structure formation.

Tyulin developed Gedroits's ideas and made some generalizations on them in 1948. In connexion with the formation of water-stable aggregates, Tyulin paid special attention to highly dispersed organic colloids. He developed a method for the fractional peptization of soil by means of which two groups of colloids are determined: the first, isolated after the replacement of exchangeable Ca by Na, is characterized by humus substances loosely linked to the crystal lattice of the clay mineral through exchangeable Ca.

The second group of colloids, isolated after the mechanical dispersion of the soil residue, represents humus substances more firmly linked with the crystal lattice of the mineral through aluminium. According to Tyulin, colloids of the first group are most important for participation in exchange reactions in the soil and for the regulation of plant nutrition as well as for the formation of an agronomically valuable structure. This was confirmed by Vladychenskii (1939), Skvortsov (1938), Shchukina (1939) and other investigators.

The study of soil structure continues to attract the attention of investigators in various countries (Kachinskii, 1947, 1949, 1960, 1963; Antipov-Karataev, 1948; Vilenskii, 1945; Novák, 1947; Sekera, 1951; Bétrémieux and Turc, 1954; Hénin, Robichet and Jongerius, 1955; Khan, 1957, 1959; and others). The results of these investigations indicate the complex mechanism of the process of structure formation and reveal a complex of conditions (mechanical and mineralogical composition of the soil, nature of the humus, character of the interaction between the minerals and the organic part of the soil, moisture conditions and the effect of agricultural machinery on the soil, etc.).

In soils of various types, the structure of the soil aggregates differs, depending both on the nature of the humus and on the mineral part of the soil. Antipov-Karataev, Kellerman and Khan (1948, 1960) successively removed separate fractions of organic substances from soil aggregates, and by microscopic analysis discovered the following characteristic differences in the structure of aggregates from various soils. In chernozems and dark-

gray forest soils, primary aggregates (micro-aggregates) are formed with calcium humates; these primary aggregates are linked to minerals of the montmorillonite type by intermicellar bonds of organic matter, forming macro-aggregates. In podzolic soils and krasnozems, the principal cementing factors are compounds of sesquioxides (mainly Fe_2O_3) with fulvic acids. Gray (and brown) forest soils are intermediate: together with humic acids linked to calcium, fulvic acids linked with R_2O_3 also occur.

Kellerman (1959) extended this work and found that when the aggregates are mainly cemented by fulvic acids and their compounds with sesquioxides, the aggregates, which are uniformly impregnated with organic matter, have a shiny appearance. Such appearance of the aggregates is characteristic of krasnozems and podzolic soils. The aggregates in chernozems and to some extent in gray forest soils are characteristically porous, probably due to a non-uniform distribution of the organic "cement", that is, humic acids with their mobility limited by coagulation with calcium.

These observations by Kellerman are in accord with our own work characterizing the nature of humus substances in various soil types (see Chapter 2). It will be recalled that humic acids from chernozems and dark gray forest soils are relatively immobile and easily coagulated with CaCl_2 . These characteristics explain the non-uniform distribution of organic substances in the aggregates from chernozems and gray forest soils observed by Kellerman. In podzolic soils and krasnozems, fulvic acids and humic acids weakly coagulated by CaCl_2 predominate in the humus composition; this may explain the uniform impregnation of the aggregates with humus substances in this group of soils, imparting to them the slimy appearance.

The work of Khan (1957, 1959) and Kawaguchi and Kita (1957) likewise indicates the role played by the humus content and the nature of the humus substances in the process of structure formation.

Turning now to the practical methods for producing a good soil structure we should mention that the sowing of perennial grasses is one method for accomplishing this, provided their growth is good. The selection of the grasses and their position in the rotation should be decided after considering the natural and economic conditions of the farm. Various other methods (the application of organic manures, the sowing of annual grasses) also bring about the improvement of soil structure to some extent, but they are less effective than the sowing of perennial grasses.

In recent years, methods of improving soil structure involving the application of cementing substances have been developed. In the USSR, this

idea emerged in the 1930's at the Institute of Physical Agronomy of Lenin's All-Union Academy of Agricultural Sciences (Kolyasev and Vershinin, 1935; Vershinin, 1937, 1953, 1958). Various methods for the artificial formation of soil structure by using industrial by-products possessing the properties of hydrophilic colloids were presented. Among these products were cellulose (viscous), hemicelluloses (xylan), lignin, bitumen substances from peat, resinous gums and also peat humic acids. However, the fact that these substances were recommended for use in enormous quantities hindered their extensive application.

In post-war years, American investigators have recommended the use of synthetic structure-forming agents representing polymeric compounds — derivatives of polyacrylic acids, which are usually referred to under the collective name of "krilium". Being hydrophilic colloids, these substances behave similarly to the polyuronides of plant residues and particularly of bacterial slimes, and favour the formation of a water-stable soil structure.

Flaig and Beutelspacher (1954, see also Flaig 1953a, b) consider that the positive effect of krilium is explained by the linear form of molecules of uronic acid; because of this they are readily sorbed by clay minerals, and, being closely interlaced with them, promote the formation of structural soil crumbs. According to these investigators, the role of humic acids, which are sphero-colloids, in soil-structure formation is more limited.

However, results from investigations by a number of authors (Antipov-Karataev and Kellerman; Kullman, Koepke and Deuel; and others) do not agree with this conclusion; according to these authors, the most important role in the formation of soil structure is played by strictly humus substances.

The mode of linkage depends essentially on the nature of both mineral and polymer, and this has been demonstrated by a number of authors. Thus Emerson (1960, 1963) has shown that polyvinyl alcohol (PVA) and cetyl trimethyl ammonium bromide (CTAB) react with the basal surface of montmorillonite and penetrate between individual silicate layers, forming interlamellar complexes. However Na-alginate or polyacrylamide tended to suppress intercrystalline expansion. Polyuronides interact with bentonite through the double oxygen bonds of the carbonyl group in the organic substance and the hydrogen atoms of the clay lattice (Kohl and Taylor, 1961).

Because only small additions (0.001–0.1 per cent of soil weight) of artificial structure-forming agents are necessary for their action, Vershinin (1958) considers that they cover the soil particles in a monomolecular layer.

In this instance it is obvious that a chemical link is formed between the polymer and the clay.

Whatever the mechanism by which polymers interact with the mineral part of the soil, they have, in many cases, a considerable effect on soil structure.

The effectiveness of artificial preparations of the polyacrylonitrile type in structure forming may be judged from the experiments by Kachinskii and co-workers (1961); pulverized soils (a sod-podzolic soil and a light chestnut soil) acquired a structural appearance when the preparations were added at the rate of 0.3–0.4 per cent of soil weight. Other preparations (e.g. NH_4 ligno-sulphonate) are required at a rate of 0.5–1.0 per cent. Only the smallest amount of the preparations Separan and VAMA were necessary. When a synthetic polymer of the polyacrylamine type, K-4, was used on serozems, good structure was obtained (Gussak *et al.*, 1961).

The preservation and duration of structure created by polymers, and the possible re-establishment of structure after mechanical damage are problems which need fuller investigation; the economics of the production and effectiveness of artificial structure-forming substances also require more precise study.

In summarizing the role of organic substances in structure formation, it should be mentioned that a number of important problems in this connexion are still obscure. Studies on the forms of link occurring between mineral constituents of the soil and organic substances, on the establishment of the relationship between the mechanical and mineralogical composition of the soil and the nature of the structure, also the more detailed study of aggregate structure by means of microscopic methods (Kubiena, 1938; Nikol'skii, 1942; Antipov-Karataev *et al.*, 1948; Pol'skii, 1949, 1952, 1955; Altemüller, 1956) will no doubt enable us to develop existing ideas on the nature of soil structure and its importance in soil fertility.

SOIL ORGANIC MATTER AS A SOURCE OF CARBON, NITROGEN AND MINERAL PLANT NUTRIENTS

Plants utilize the elements of carbon, nitrogen, and mineral nutrients under conditions in which substances are cycled by biological and geological processes. These elements, scattered through the atmosphere, the hydrosphere and the earth's crust, are accumulated by autotrophic and heterotrophic organisms in the form of living substance and are subsequently liberated during living processes and after the death of the organism.

This is a biological cycle of immense scale and significance, occurring, according to Williams, within the trajectory of the geological cycle.

The admission of nutrients from the great (geological) cycle into the small (biological) cycle, and the reverse process, does not have the character of a closed cycle. The decomposition of plant and animal organisms after death does not proceed completely to final products of mineralization, but is accompanied by the new formation of organic substances, in many cases of complex nature (peats, coals, sapropels, oils, humus substances of the soil), possessing a greater resistance to decomposition than did the original organic substances.

The reserve of organic carbon in these formations, including also the organic substances of living organisms and their dead residues, totals 6×10^{15} or 6000 billion tons (Nichiporovich, 1955, 1956).

According to existing calculations (Lundegårdh, 1924, 1927, 1931, 1937; Vernadskii, 1934; Ūspenskiĭ, 1956), astronomically large reserves of carbon dioxide and carbon in inorganic and organic forms are present on the Earth—in the atmosphere, in the waters of oceans and seas and in the soil crust.

However, the principal source of the carbon dioxide required by plants during photosynthesis is the atmosphere, where the CO_2 content is approximately 0.03 per cent or about 0.57 mg per l of air and its reserve, about 2.1 billion tons. When one considers that land plants of the earth fix annually, during photosynthesis, about 20,000 million tons of carbon (or approximately 80,000 million tons of CO_2), then the total carbon-dioxide content of the atmosphere would be sufficient to last only for a few decades.

But it is a well known fact that the CO_2 of the air is continually being replenished from other reserves, including the hydrosphere, the surface of which mingles freely with the atmosphere. In the air and in the waters of the Earth the total amount of carbon dioxide available to land plants exceeds (according to Vernadskii) 10^{14} tons, which is sufficient to satisfy the carbon-dioxide requirement of plants for thousands of years. The most important source of replenishment of the carbon dioxide of the atmosphere is the soil. According to an approximate calculation by Ūspenskiĭ, the total amount of CO_2 produced in one year through the respiration process of heterotrophic populations of the soil is represented by the following values:

Soil invertebrates	3.7×10^9 tons
Bacteria	51.4×10^9 tons
Fungi	8.8×10^9 tons
Total:	<u>63.9×10^9 tons</u>

To this should be added carbon dioxide produced during the respiration of plant roots, which amounts to 71.5×10^9 tons annually. The total annual amount of carbon dioxide of biological origin formed in the soil is 13.5×10^{10} tons, which generally corresponds to the total annual requirement of land plants on the Earth (80,000 million or 8×10^{10} tons of CO_2).

It would seem that the plant, having at its disposal enormous, systematically supplemented resources of carbon dioxide in the atmosphere, is sufficiently provided with it. However, it was found that during the course of the day, particularly during the hours of intensive photosynthesis, there may occur a time when the carbon-dioxide concentration in the air layers surrounding the plant is lower than normal and this will result in a decrease in the intensity of photosynthesis.

Therefore, the problem of the uninterrupted supply of carbon dioxide to the plant should not be disregarded from the point of view of agriculture; in this connexion, the soil, being the nearest source of carbon dioxide most available to the plant, has a most important role.

A means of ensuring the production of carbon dioxide by the soil is by the systematic supplementation of its reserves of fresh organic matter.

Considerable reserves of plant nutrients are accumulated in the composition of soil humus; for such important elements as nitrogen and phosphorus the amounts can be reckoned in tons. Data on the content of humus, nitrogen and phosphorus in the cultivated layer and in the top metre layer of soil for the main soil groups of the USSR are presented in Table 34.

Most of the nitrogen in the upper soil layers is organic; this view, expressed years ago by many workers (Jodidi, 1910–13; Shmuk, 1914; Lathrop, 1916; Kudryavtseva, 1924) is now firmly established. However, in the lower horizons, a substantial part of the nitrogen is present as $\text{NH}_4\text{-N}$ sorbed by the crystalline lattice of clay minerals (Stevenson, 1958, 1959, 1960b; Bremner and Harada, 1959; Bremner, 1959). Therefore the narrow C:N ratio of 5 or less that is often observed in the lower horizons of a soil profile does not necessarily indicate that the nitrogen is necessarily organic in origin. Stevenson associates the presence of nitrogen in the lower layers with the previous history of the Earth; he maintains that atmospheric precipitation was the source of nitrogen, which entered and was fixed by the rocks before their transformation into soil.

There undoubtedly are in soils some free amino acids which are formed during the decomposition of organic residues and are metabolic products of micro-organisms. Chromatographic analysis of soil solutions

TABLE 34. RESERVES OF ORGANIC MATTER, ORGANIC NITROGEN, PHOSPHORUS AND SULPHUR IN SOILS OF USSR IN TONS PER HECTARE

Soils	Humus in layer*		Nitrogen in layer*		P ₂ O ₅ in cultivated layer†		SO ₃ org. in cultivated layer ‡
	0-20 cm	0-100 cm	0-20 cm	0-100 cm	mineral	organic	
Podzolic soils	53	99	3.2	6.6	1.27-1.44	0.56-0.63	0.34-0.78
Forest steppe podzolized soils	109	215	6.0	12.0	1.72	1.32	0.55
Leached chernozems	192	549	9.4	26.5	—	—	0.69
Deep chernozems	224	709	11.3	35.8	2.87	1.56	—
Ordinary chernozems	137	426	7.0	24.0	—	—	0.50
Dark chestnut soils	99	229	5.6	—	2.09	0.63	1.10
Serozems	37	83	2.5	7.5	1.68-1.91	0.30	1.00
Krasnozems	152	282	4.7	10.5	—	—	—

* From Tyurin (1949)

† From Kheifets (1950)

‡ From Vinokurov (1937)

and extracts has shown that the following amino acids are present: aspartic acid, glutamic acid, alanine, serine, valine, leucine, lysine and others.¹

However the content of these amino acids in soils is not high and is usually in the range from several microgrammes per kilogramme of soil to ten times this amount.

A considerable part of the nitrogen can be dissolved by hydrolysis of the soil with 6N HCl; a great number of amino acids have been discovered in the hydrolysate (Kojima, 1947; Bremner, 1949, 1950; Sowden and Parker, 1953; Sowden, 1955, 1956, 1957; Stevenson, 1954, 1956; Young and Mortensen, 1958).

These amino acids can be determined quantitatively by chromatography; the most common are aspartic acid, glutamic acid, glycine, lysine, proline, threonine, serine, alanine, valine, histidine, leucine and iso-leucine, tyrosine and phenylalanine. The α -amino acid nitrogen in the hydrolysate may amount to as much as two thirds of the total soil nitrogen.

In contrast to α -amino acids, diamino acids in the acid hydrolysate of the soil amount to only 4-6 per cent of the total soil nitrogen. In addition to this a certain amount of soil nitrogen is represented by amino-sugars (Bremner and Shaw, 1954; Bremner, 1958; Stevenson, 1957).

¹ See Chapter 2, section "Organic Substances of an Individual Nature."

About one third of the soil nitrogen is not hydrolysed; this part consists of heterocyclic forms or nitrogen compounds firmly linked with the mineral part of the soil. This so-called humin nitrogen is the least mobile form of soil nitrogen.

In the arable layers of podzolic soils there is about 0.5 ton per hectare of organic phosphorus, in chernozems there may be as much as 1.5 tons per hectare (see Table 34). The nature of soil organic phosphorus is not yet fully clear. Phytin, the calcium-magnesium salt of inositol hexaphosphoric acid, is the commonest form of organic P_2O_5 ; it constitutes 30–80 per cent of the total soil organic phosphorus. In a second group are included nucleic acids, which amount to approximately 10 per cent of the total organic P_2O_5 ; among these deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), obviously of microbial origin, have been identified. Some organic forms of phosphorus can be assimilated by plants, either directly (Shulov, 1913) or after splitting by enzymes occurring in the root exudates of plants.

Very little is known about organic forms of sulphur in soils; in the USSR, Vinokurov (1937), Madanov (1946) and Aidinyan (1957) have studied this problem. We have calculated the reserves of organic sulphur from Vinokurov's data and the values, given in Table 34, are of the same order as for organic P_2O_5 .

Organic sulphur is derived mainly from plant and animal residues and also from the cytoplasm of micro-organisms in which sulphur is component of various compounds such as proteins and amino acids. The humification of these residues may explain the presence of sulphur containing amino acids—methionine and cysteine—in humus substances.

As can be seen from Table 34, the nitrogen reserves of the soil are very large and in some cases (in chernozems) are sufficient to satisfy plant requirements for hundreds of years without external supply. However, agricultural production cannot continue indefinitely with the mobilization of soil reserves. One should bear in mind that a large part of the soil nitrogen is present in the composition of humus substances and therefore a continuous mobilization of nitrogen reserves is inevitably associated with an intensive destruction of humus; this results in a deterioration of physical and physicochemical properties—the loss of soil structure, decrease in exchange capacity, etc. Therefore, a decrease in soil fertility in a system of agriculture based only on natural fertility is inevitable long before the nutrient reserves are exhausted.

Under agriculture, the nutrient cycle is complicated by the action of man and domestic animals. The plant takes up nutrients from the soil

and from the atmosphere; however, only a part of these nutrients is returned to the soil in the form of leaf-fall, stubble and root residues and as farmyard manure from the part removed after the harvest. A large part of the nutrients removed with the crop at harvest is distributed on the surface of the Earth or enters the atmosphere as products of the activity or as wastes of man and animals.

In Table 35 data are given which show the amount of nutrients removed by the crop and the amount remaining in the soil as root residues; the estimation was made on the basis of a good yield.

With a cereal yield of 16–20 quintals per hectare, 55–75 kg of nitrogen and 20–30 kg of phosphorus are contained in the grain and straw and 14–20 kg nitrogen and 12–16 kg phosphorus in the root residues. Therefore, only about a quarter of the total amount of nutrients taken up by the plants is returned to the soil in the composition of roots.

The balance of nutrients on cotton fields is even less favourable: here the recovery of nitrogen and phosphorus by the soil occurs only in the form of the highly lignified cotton roots remaining in the field, which contain negligible amounts of these elements. Suffice it to say, that for every 10–15 kg nitrogen contained in the mass of cotton roots, 80–100 kg are removed with the cotton crop and as aerial parts.

These calculations show fairly clearly the quantitative relationship between the amount of nutrients taken up by the plants and the amount left behind as root residues.

Of course, the return of plant nutrients is not limited only to the mass left behind by the plants; it is also necessary to take into account the return of nitrogen, phosphorus and other elements during the growth of the plant by way of root exudates, the composition of rootlets and root hairs which die off during growth. An item of income in the balance is the provision of plant elements from soil material and of nitrogen from the atmospheric precipitation. An essential role in the nitrogen balance is played by the free-living bacteria which fix atmospheric nitrogen. But even when all means of return are taken into account (see Gericke, 1945, 1946; Vetter, 1953, 1955; Tyurin, 1956), there is still in the annual balance of nutrients under cereals, a deficit of several kg per hectare. The obvious discrepancy in these values once again emphasizes the need for applying organic and mineral fertilizers and for the introduction of leguminous mixtures. To illustrate this, some data characterizing the nitrogen content of a leguminous crop and the amount of nitrogen left behind in the soil will be given (Table 36).

The first example (clover) was worked out for the sod-podzolic soil

TABLE 35. TOTAL CONTENTS OF NITROGEN AND PHOSPHORUS REMOVED WITH CROP AND REMAINING IN ROOTS OF AGRICULTURAL CROPS

Plant	Yield (q/ha)	Content in crop					Amount of root residue (q/ha)	Content in roots			
		N		P ₂ O ₅				N		P ₂ O ₅	
		%	kg/ha	%	kg/ha	%		kg/ha	%	kg/ha	
Cereals: grain straw	16-20	2.5	40-50	0.6-0.8	10-16	20	0.7-1.0	14-20	0.6-0.8	12-16	
	25-30	0.6-0.8	15-24	0.5	12-15						
	—	—	55-74	—	22-31						
Total:		—	—	—	—	—	—	—	—	—	
Cotton: with a yield of raw material of 16-20 q/ha*	—	—	80-100	—	16-20	20-30 †	0.5	10-15	—	—	
	—	—	—	—	—						

* Data from Kudrin (1947) † Data from Rozanov (1950)

TABLE 36. AMOUNT OF NITROGEN AND PHOSPHORUS IN AERIAL MASS AND IN ROOT RESIDUES OF LEGUMINOUS PLANTS

Plant	Total yield (q/ha)	Content in aerial mass				Amount of root residue (q/ha)	Content in roots			
		N		P ₂ O ₅			N		P ₂ O ₅	
		%	kg/ha	%	kg/ha		%	kg/ha	%	kg/ha
Clover: two years' utilization Lucerne: 3 years' utilization (Dorman <i>et al.</i> 1949) Lucerne: 3 years' utilization (Belyakova, 1947)	100	2.0-2.5	200-250	0.5	50	50	2.0-2.5	100-125	0.4-0.9	20-45
	370	—	960	—	200		2.0-2.5	200-300	—	40-100
	520-660	—	1300-1600	—	260-330		2.0-2.5	400-500	—	80-180

zone. With a total clover yield over two years of 100 q/ha, the amount of nitrogen in the whole plant mass was 300–375 kg, of which 100–125 kg was returned to the soil in the roots. These values have approximately the same order of magnitude as those given by D. N. Pryanishnikov in the book *Nitrogen in the Life of the Plant and in the Agriculture of the USSR* (1945).

Legumes play a very great part in nitrogen accumulation under the irrigated conditions of Central Asia: this can be seen from the data of Table 36, calculated from the recent results of experimental establishments. According to Dorman (1949), lucerne provides 4–5 cuts annually, which, over 3 years, amounts to 37 tons of hay per ha; this contains 960 kg nitrogen and about 200 kg of phosphorus. Lucerne leaves behind 10–12 tons of roots, containing 250–300 kg of nitrogen and 40–50 kg of phosphorus.

Still higher figures for the nitrogen accumulated by lucerne are given by Belyakova (1947); according to her data the nitrogen content of a crop of hay over 3 years is approximately $1\frac{1}{2}$ tons/ha; in addition to this the roots contain 400–500 kg/ha of nitrogen.

Besides accumulating nitrogen in the growing mass, legumes also enrich the soil in nitrogen. For the conditions of Central Asia, a number of authors (Ioffe, 1930; Kudrin, 1936; Meerson, 1939; and others) estimate the increase of soil nitrogen due to the introduction of lucerne, as several hundred kg/ha. From these examples, it can be seen that the role of leguminous plants in accumulating nitrogen increases as yields increase (Sokolov, 1957).

THE EFFECT OF ORGANIC MATTER ON THE GROWTH AND DEVELOPMENT OF PLANTS

Mulder detected the presence of organic acids of low molecular weight (formic, acetic, propionic, aspartic, etc.) in the soil and observed that they promoted plant growth; poor growth occurred in soils in which these compounds were absent.

Schreiner, who separated various organic substances of a non-specific nature from the soil and tested their effect on the plant, found that in water cultures some of them, e.g. vanillin, benzoic acid, some aldehydes and dihydroxystearic acid, inhibited plant development even at low concentrations.

Since then, many investigators have observed a positive or negative effect of various chemically individual organic substances and also of

strictly humus substances on the plant, but the mechanism of this phenomenon is not clear.

In Bottomley's experiments (1914) peat inoculated with bacteria had a positive effect on plant growth in soil and in water cultures. He attributed this effect to the presence in the peat of substances of auxin type, which had an effect similar to that of vitamins in the living animal. Mock-eridge (1924) found that water-soluble humus substances from farmyard manure and from rotted leaves had a positive effect on the growth and development of the plant and on certain biological processes — nitrification and nitrogen assimilation; the effect of these substances increased as the decomposition of organic residues increased.

The work of Hillitzer (1932) should also be mentioned. After observing the vigorous root production by plants in the presence of water-soluble humus substances, he thought, like Bottomley, that humus substances were acting as auxins. Similar views were expressed by Chaminade and Boucher (1940), who observed a positive effect of extracts of garden soil, peat and ivy on *Pelargonium* cuttings.

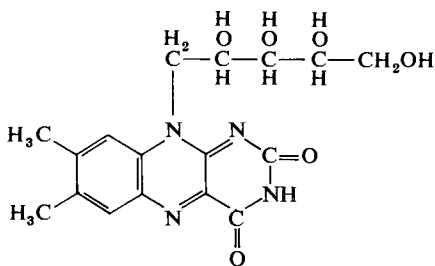
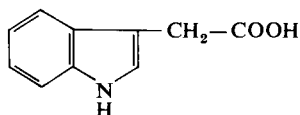
It was established that farmyard-manure application increased the germination capacity and also the vitamin content of plants; animals given fodder from these fields showed a higher resistance to sickness (see Tyurin, 1937 and Waksman, 1936). These phenomena were directly connected with the presence in farmyard manure of certain organic compounds of the vitamin type. In recent years Starkey (1942), Stewart and Anderson (1942) and Carpenter (1943) separated vitamins of the pantothenic-acid and riboflavin type from soils, composts, various plant residues and cow manure.

Some investigators, however, expressed different views. Olsen (1930), for instance, attributed the positive effects of humus substances on the plant to the presence in them of available iron. Lieske (1932, 1935), who investigated the possibility of using brown coal as a fertilizer, concluded that the effect of the coal is due to the free humic acids which it contains. From his experiments with duckweed, Lieske concluded that humic acids and their derivatives increase the permeability of plant membranes, so promoting the uptake of nutrients.

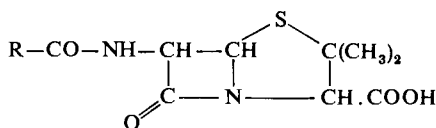
Vitamins, auxins and antibiotics in the organic part of the soil

It has been found that substances possessing biological activity are present in the organic part of the soil.¹ These are auxins and vitamins entering the soil in the root exudates of plants, in farmyard manure, in compost and in plant residues, and they are also produced in large amounts by the living population of the soil.

These groups of biologically active substances, which also include antibiotics, are very diverse and complex in nature, as the following examples of their structural formulae show:

Riboflavin (vitamin B₂)

Indole-3-acetic acid (heteroauxin)



Penicillin (antibiotic)

A diversity of vitamins is particularly characteristic of fertile soils, in which the following have been found: vitamins B₆ and B₁₂, pantothenic acid, folic acid, nicotinic acid, p-aminobenzoic acid, riboflavin, biotin and others. The content and distribution of vitamins in the soil are shown in Table 37.

¹ Literature on this subject is cited in the following publications: Krasil'nikov (1952, 1958); Ovcharov (1953); Rakitin (1953); Schopfer (1943); Audus (1949); Schmidt (1951); Fischnich (1955); Lochhead (1958).

TABLE 37. THE VITAMIN CONTENT OF THE SOIL (Mishustin, 1956)

Vitamin	Vitamin content per kg soil	Vitamin	Vitamin content per kg soil
Thiamine	2.9 — 19.3 μ g	B ₁₂	2.0 — 15.0 μ g
Riboflavin	0.09 — 9.8 mg	B ₆	4.0 — 14.0 μ g
Biotin	0.023 — 0.62 μ g	Nicotinic acid	0.1 — 0.35 mg

According to Krasil'nikov, the vitamin content, like the bacterial content, depends upon the soil type. Micro-organisms are the main producers of vitamins in the soil; Meisel' (1950) has calculated that soil micro-organisms can produce from several hundred grammes to 1 kg of the B group vitamins in one year per hectare of fertile soil. Amounts of vitamins synthesized by cultures of micro-organisms are given in Table 38.

TABLE 38. SYNTHESIS OF VITAMINS BY CULTURES OF MICRO-ORGANISMS (in μ g/g cell dry matter) (Mishustin, 1956)

Culture	Thiamine	Nicotinic acid	Vitamin B ₆	Biotin
<i>Pseudomonas aurantiaca</i>	203	355	91	162
<i>Pseudomonas fluorescens</i> (No. 1)	23	511	16	21
<i>Pseudomonas herbicola</i>	15	470	12	9

Although a plant organism can independently synthesize in its tissue the vitamins necessary for itself, a supplementary supply of vitamins may have a substantial positive effect on the plant. Shavlovskii (1954) and Ratner and Dobrokhotova (1956) have shown that it is possible for plants to take up vitamins from the external medium through the root system. The part played by vitamins on the enzymic activity and on the metabolism of plants is illustrated by the work of Chailakhyan (1956) and of Ratner (1958).

Related to the group of biologically active substances are the growth promoting substances, the auxins. According to Krasil'nikov (1958), auxins are present in soils in approximately the same amounts as vitamins;

they also enter the soil in similar ways (as plant components and products of microbial activity).

A typical soil auxin-heteroauxin (indole-3-acetic acid)—is a product of the activity of numerous soil micro-organisms, in particular *Azotobacter* (Smalii, 1948). Heteroauxin acts on the plant by stimulating the development of the root system and the aerial organs and also by accelerating the ripening of fruits (Turetskaya, 1949; Verzilov, 1949).

The interesting biological stimulators, the gibberellins, are produced by the fungus *Gibberella fujikuroi*, of which the fungus *Fusarium moniliforme* is a conidial stage. Recently gibberellins have been detected in the products of the activity of actinomycetes and of some cultures of soil yeasts (Krasil'nikov *et al.*, 1958). Gibberellins stimulate growth and flowering in certain plants and influence their metabolism. It should be noted that vitamins and growth stimulators only affect the plant positively at low concentrations.

Certain low-molecular-weight organic acids, in particular dicarboxylic acids such as succinic, cinnamic, fumaric and other acids possess growth promoting properties (Blagoveshchenskii *et al.*, 1945, 1955, 1959). In low concentrations these substances have a positive action on the energy of seed germination, on the growth of roots and aerial organs and on the yields and quality of the crops.

Such physiologically active organic substances of an individual nature are present in aqueous extracts of fresh and decomposing plant residues (Flaig and Saalbach, 1959b; Flaig *et al.*, 1960) and in soil solution (Kononova and D'yakonova, 1960), which may explain the positive effect on the plant of these extracts and solutions when they are added in low concentrations to the nutrient media.

Together with vitamins and growth promoting substances, antibiotic substances are produced in the soil by micro-organisms. This group includes streptomycin, globisporin, penicillin, aureomycin, terramycin and others; the observed activity of these substances depends on the soil characteristics (Krasil'nikov, 1958), for instance, the nature of the humus (Bekker, 1959). Antibiotics can be taken up by plants, as has been demonstrated by Krasil'nikov (1952, 1958) and Winter and Willeke (1951). The substantial size of antibiotic molecules (molecular weight 300–500 or higher) does not prevent their penetration into the plant in an unchanged form (Krasil'nikov, 1958; Scheffer and Kloke, 1956).

Extracts and juices of numerous plants possess antimicrobial properties (Runov and Enikeeva, 1955; Mishustin and Naumova, 1955; Winter, 1955; Kaunat, 1957; Nielsen *et al.*, 1960; Guenzi and McCalla, 1962).

It appears that phytoncides (volatile antimicrobial substances) are related to this group (Tokin, 1948, 1951). Consequently substances having the properties of antibiotics not only affect plants but may also influence the composition of microbial populations in the soil.

The study of soil vitamins, growth promoting substances and antibiotics requires further attention. It is particularly important to develop methods for using them in practical agriculture to accelerate the growth of crops and the ripening of fruits, and to protect plants from disease.

Physiological properties of strictly humus substances

Of great interest are the works which show convincingly that strictly humus substances have an effect on plant development. Of these works, we should mention first the investigations of Blagoveshchenskiĭ and Prozorovskaya (1934), Prozorovskaya (1936), Niklewski and Wojciechowski (1937).

In experiments with soil, sand and water cultures, these investigators showed that, in the presence of small amounts of humic-acid gel from peat, the nutrient uptake of the plant was increased and better growth resulted. Some data from these works are given in Tables 39 and 40.

TABLE 39. GROWTH OF FLAX IN WATER CULTURES WITH HUMIC ACIDS
(Prozorovskaya, 1936)

Treatments	Stem length (cm)		Root length (cm)	Dry weight of green mass (g)	Dry weight of roots (g)
	Total	Productive			
NPK	50	43	17	3.2	0.7
NPK +20 mg humic acid	65	50	18	5.1	0.9
NPK +200 mg humic acid	62	48	19	4.7	0.9

In Table 40 data are given characterizing the amount of nitrogen, phosphorus and potassium in the flax yield in this experiment.

In seeking an explanation of the positive effect of humic acids on plant growth, Prozorovskaya (1936) demonstrated that the exosmosis of sugars from bulb scales increased in the presence of humic acid. In experiments on the infiltration of NH_4NO_3 into sunflower leaves, the presence of humic acid was found to increase the percentage content and total amount of

TABLE 40. CONTENTS OF NITROGEN, PHOSPHORUS AND POTASSIUM IN FLAX CROP (Prozorovskaya, 1936)

Investigated elements	In green mass with treatments:		In roots with treatments:	
	NPK	NPK + 200 mg humic acid	NPK	NPK + 200 mg humic acid
Nitrogen (%)	2.02	2.45	2.15	3.00
Total amount of nitrogen in mg per pot	128	190	17	30
K ₂ O (%)	2.56	2.96	2.98	3.21
Total amount of K ₂ O in mg per pot	162	230	25.6	33.6
P ₂ O ₅ (%)	0.96	0.93	2.61	2.62
Total amount of P ₂ O ₅ in mg per pot	59	75	19	27

nitrogen. From these observations, Prozorovskaya considers that humic acids in small amounts act as specific sensitizing agents, increasing the permeability of the plasma and resulting in an increased uptake of nutrients by the plant; in large amounts humic acids are a source of available iron.

During the last decade, the problem of the effect of humus substances on the plant has attracted a great deal of attention from investigators. It is remarkable that the investigations carried out by scientists of different countries (Prát—Czechoslovakia; Niklewski, Gumiński—Poland; Khristeva—USSR; Chaminade—France; Flaig—W. Germany; and others) should be complementary to each other, revealing main aspects of the nature of this complex phenomenon, extremely important both from a theoretical and from a practical standpoint.

Systematic studies on the effect of humus substances on growth and on the application of humic fertilizers for increasing yields were carried out in the USSR by Khristeva *et al.* (1947, 1948, 1949, 1950, 1951, 1953, 1955, 1957, 1958, 1962).

In a large number of experiments with different plants, Khristeva found that small amounts of humic acids from carbonaceous shales, peats or soils increased plant growth and development. Especially clear results were obtained in sand and water cultures. The positive effect of introducing humic acids increased with increasing concentration from 0.00006 to 0.006 per cent which, from her calculations, is 0.026 g of molecularly soluble humic acid per kg soil. A further increase in the concentration had a nega-

tive effect on growth (Table 41). The strongest positive effect was obtained in experiments with cereals and the weakest effect was with legumes. In experiments with oil plants no effect of humic acids was obtained.

TABLE 41. EFFECT OF VARIOUS DOSES OF HUMIC ACIDS ON WHEAT (Khristeva, 1949)

Experimental treatment	Length of primary root				Length of stem	
	1st measurement		2nd measurement			
	mm	%	mm	%	mm	%
Water	63 ± 5	100	65 ± 2.2	100	92	100
0.00006 % potassium humate	62 ± 3.2	98	56 ± 1.5	86	112	122
0.0006 % potassium humate	83 ± 7.9	131	111 ± 7.5	171	125	136
0.006 % potassium humate	80 ± 7.5	127	109 ± 7.5	168	135	147
0.06 % potassium humate	57 ± 5.5	90	79 ± 7.0	121	127	138

Data on the effect on sodium humate on the development of different plants are given in Table 42.

TABLE 42. EFFECT OF SODIUM HUMATE ON VARIOUS PLANTS (Khristeva, 1949)

Plant and experimental treatment	Primary roots length (mm)	Secondary roots length (cm)	Length of stem (mm)
Spring wheat:			
Lutescens 62:			
water	68 ± 11	1	139
sodium humate	200 ± 23	30-40	192
Melanopus 1387:			
water	152 ± 18	1	210
sodium humate	240 ± 21	20-30	210
Winter wheat:			
Ukrainka:			
water	75 ± 11	1	201
sodium humate	378 ± 46	10-100	232
Voroshilovskaya:			
water	61 ± 8	—	151
sodium humate	325 ± 48	10-60	209
Rice 87:			
water	90 ± 7	—	140
sodium humate	152 ± 12	—	171

Khristeva believes that humic acids entering the plant at early stages of development are a supplementary source of polyphenols, which function as respiratory catalysts. This results in an increase in the living activity of the plant: enzyme systems are intensified, cell division is accelerated, root systems show greater development and, ultimately, the yield of dry matter increases.

Khristeva (1950, 1951, 1953) provided evidence for the participation of humic acids in plant respiration; after the injection of humic-acid sol into plant tissues, she observed (using a Warburg apparatus) an increased intensity of oxygen absorption by plant tissue. Khristeva believes that humic acids, because they contain quinone groups, are hydrogen acceptors and, at the same time, activators of oxygen.

Biber and Magaziner (1951) observed an increase in the respiration of isolated plant tissues under the influence of small doses of humic acids. The observations of Biber and Bogolyubova (1952) on the acceleration of wound healing in rabbits after the injection of humic-acid solutions into the tissues deserve attention.

In our laboratory, Pankova (Kononova and Pankova, 1950) carried out a number of experiments to investigate the effect of humic acid on the plant. For this purpose, Pankova, like Khristeva, used dialysed sodium humates and humic acids in the form of highly dispersed sols and molecular solutions. The experiments were carried out in liquid media consisting of distilled water and humic acid solution, the carbon of humic acid being present at concentrations of 4×10^{-6} or 5×10^{-6} g per ml of the medium. Increasing concentrations increased the positive effect on growth, although at high humate concentrations a decrease in the positive effect was observed.

TABLE 43. EFFECT OF HUMIC ACIDS ON GROWTH OF MAIZE (Pankova's experiments)

Experimental treatments	Total number of roots of two plants		Total length of roots of two plants (cm)	
	after 14 days	after 24 days	after 14 days	after 24 days
Control (distilled water)	29	21	72	90
Humic acids from podzolic soil	25	43	178	250
Humic acids from chernozem	26	37	168	188
Sodium humate from chernozem	34	40	262	300

The range of optimum concentration varied somewhat in different plants.

The set-up in these experiments was two plants per pot and an experimental period of 12–24 days; at the end of the experiment, the number of roots was counted and their total length measured. Some of the results are given in Table 43.



FIG. 47. The development of maize roots.

1. In the presence of fulvic acids; 2. In the presence of Na-humate (from chernozem);
3. Control.

As can be seen from Table 43, humus substances have a definite positive effect on the development of the root systems of maize (Fig. 47) and even eliminate the deleterious effect of distilled water. Similar results were obtained in an experiment with wheat (Table 44).

Pankova's experiments demonstrating the regeneration of seedling roots are of particular interest. Rootlets were cut off after 6–7 days' growth and the seedlings were then placed in a humic-acid solution containing 4×10^{-6} g per ml carbon of humic acid. After a certain period, an abundant regrowth of rootlets was observed; a similar effect was also seen after a second cutting of the regrown roots. Pankova's observations on the cereal *Panicum* (sp?) are also of interest. After removing the roots and placing

TABLE 44. EFFECT OF HUMUS SUBSTANCES ON GROWTH OF WHEAT (Pankova's experiment)

Experimental treatments	Total number of roots of two plants		Total length of roots of two plants (cm)	
	after 14 days	after 24 days	after 14 days	after 24 days
Control (distilled water)	25	25	22	22
Humic acids from chernozem	22	28	91	125
Sodium humate from chernozem	11	15	81	115

the seedlings in an aqueous solution of humic acid, an abundant regrowth of roots from the internodes was observed after a certain time. In the control vessels containing water the roots did not regrow (Fig. 48).

The manifold effect of humus substances on the plant, shown both in the external medium and in the biochemical processes occurring in the plant, has been demonstrated fairly completely by a number of contemporary investigators.

Gumiński *et al.* (1950, 1953, 1955, 1957, 1959) and Gumińska (1958) showed that humic acids regulate the oxidation-reduction condition of the medium in which the plant is growing. They found that during oxygen deficiency humates facilitate plant respiration; this they attribute to the presence in humus substances of hydroxyquinones, which function as hydrogen acceptors when the oxidation of substances is taking place in plant tissues. Smidova (1960) has shown that the respiration rate of plant roots increased when humic acid was present.

The participation of humic acids in the intra-cellular respiratory processes of the plant is of similar character. It has already been mentioned that Khristeva attributes the stimulating effect of humic acids to their participation in oxidation-reduction processes in the plant, and she associates this with the presence in humic acids of quinone groups, which are hydrogen acceptors and, at the same time, activators of oxygen.

A similar explanation of the stimulating effect of small doses of humic acids was given by Flaig and co-workers (Flaig and Otto, 1951; Otto, 1952; Flaig, Otto, Küster and Reinemund, 1954; Flaig, 1954). Humus substances entering the plant function as hydrogen acceptors and fulfil the role of dehydrases in various processes, as, for instance, during the deamination of amino-acids, etc. Furthermore, *o*-quinones have a greater physiological effect than *p*-quinones. This is in accord with the view that *o*-quinones are

intermediates in the synthesis of humic acids (Flaig and Saalbach, 1955, 1956; Flaig and Söchting, 1962).

The latest investigations of Flaig and co-workers (Flaig, Scharrer and Scholl, 1957; Saalbach, 1956; Flaig, 1958; Flaig and Saalbach, 1959; Flaig



FIG. 48. The regrowth of roots from the internodes of *Panicum* (sp.?). *Left*. Control (water); *Right*. In the presence of sodium humate.

and Scholl, 1960) indicate new aspects of the effect on the plant of small doses of humic acids and of individual organic compounds related to them (thymohydroquinone). It was found that these substances altered the carbohydrate metabolism of the plant and, in some cases, promoted

the accumulation of soluble sugars; the latter increase the osmotic pressure inside the plant and under conditions of low air humidity promote a greater resistance to wilting.

Investigations by Boguslawski and Saalbach (1960) showed that the moisture regime is important during the action of thymohydroquinone on plant productivity and utilization of fertilizer nitrogen.

The work of Rypáček (1962), Ku Tsen-Chui (1962) and Sladký (1962) has shown that humus substances influence the anatomical structure of the plant: they accelerate the differentiation of the growing point. Řerábek (1962, 1963) found that humic acids intensify the positive effect of auxin on the growth of the coleoptile segments in wheat.

It is interesting that various groups of humus substances (alcohol extracted substances, humic acids, fulvic acids) that influence plant development, respiration, chlorophyll content and metabolism, are also effective when their solutions are spread on the aerial parts of the plant (Sladký, 1959; Tichý, 1958, 1959).

Of similar interest is the action of humic acids on the physico-chemical properties of plant protoplasm. Earlier observations by Lieske and Prozorovskaya that humic acids increase the penetrability of plant membranes were confirmed by the experiments of Khristeva (1951) and Chaminade and Blanchet (1953). The viscosity of protoplasm was found to be altered in the presence of humus substances (Rypáček, 1962).

Like Prozorovskaya, a number of authors have noted changes in the requirements of the plant for the following nutrients: nitrogen (Flaig and Saalbach, 1958; Kononova and D'yakonova, 1960); phosphorus and potassium (Misterski, 1957; Pagel, 1960); calcium and phosphorus (during more advanced stages of plant development) (Peterburgskii, 1956, 1962).

These profound effects of humus substances on the biochemical and physiological processes in the plant can be explained by the ability of these substances to enter the plant. Prát has investigated this problem using ^{14}C -labelled humic acid (Prát and Pospíšil, 1959; Prát, 1960). Examining the anatomical structure of the plants by micro-autoradiography, it was possible to establish that humus substances penetrate into plant tissues; fulvic acids, having a smaller molecular size than humic acids, enter most easily. The entry of humus substances into plant tissue has also been observed by Aso and Sakai (1963).

This short review illustrates the active role played by humus substances in the physiological and biochemical processes in the plant. It is reasonably certain that small additions of these substances help to increase the respiration rate, the metabolism and the growth of the plant, causing

the plant to require more nutrients from the soil and fertilizers. This effect has recently been established by the experiments of Khristeva (1951), Chaminade and Blanchet (1953a, b), Blanchet (1958) and Chaminade (1956, 1958, 1960).

For example, in one of Chaminade's experiments rye grass was grown in sand cultures with a continuous supply of nutrient solution, the nitrogen content of which was within the range 17–137 mg/litre, and was pro-

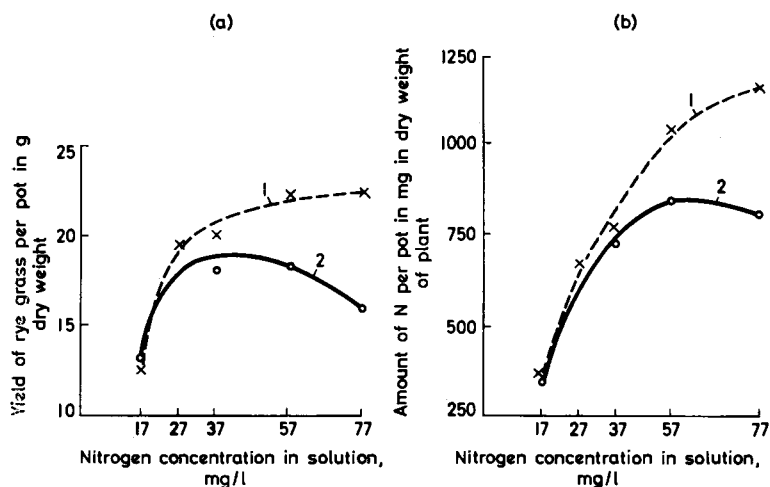


FIG. 49. The effect of sodium humate on the yield of rye grass and its nitrogen uptake (Chaminade, 1958).

(a) — yields; (b) — nitrogen uptake; 1 — with humate; 2 — without humate.

vided with minor and trace nutrients. In one series of experimental pots, the rye grass was only supplied with mineral nutrients; in another series of pots, sodium humate was added (2.5 mg/litre) to the nutrient solution.

The yields of rye grass from eight cuts taken during the growing season and the total nitrogen taken up in the eight cuts are shown in Fig. 49. These results show that in a treatment without humate, a direct relationship between yield and the amount of nitrogen applied was only found when the nitrogen was applied at low rates; high rates had an inhibitory effect on the plant. Thus, when sodium humate was present in the medium, the plant was able to utilize large amounts of mineral nitrogen which were harmful in the absence of humate.

Small additions of humus substances have a beneficial effect on micro-organisms as well as on higher plants (Remy, 1911; Krzemieniewski,

1908; Prażmowski, 1912; Iwasaki, 1930). In more recent work, the stimulating effect of small additions of humic acids on certain micro-organisms has also been recorded, for instance, on *Bac. mycoides*, *Aspergillus niger* and *Penicillium glaucum* (Kudrina, 1951). Aleksandrova found increased catalase and phenoloxidase activities in *Bac. mycoiues* and *Sorann-gium cellulosum*. Rybalkina (1957) noted an enhanced nitrogen fixation by *Clostridium Pasteurianum* when small amounts of humic acid sol were added and Isvaran (1960) discovered a similar effect with *Azotobacter*.

Summarizing many years' investigations, Prát (1955) concludes that humic acids have a positive action on algae. According to Chaminade (1955, 1960), humus substances and their aromatic precursors have a stimulating effect on *Aspergillus niger*, which he attributes to the preseoe of quinone groups and polyphenols in the humus substances. Similarly, Saalbach and Küster (1958) showed that small concentrations of polyphenol-type aromatic compounds have a positive effect on the growth of the fungi *Mucor*, *Fusarium*, *Aspergillus*, and *Penicillium*, and on bacteria, in particular those belonging to the genus *Pseudomonas*.

These observations are of the utmost importance in plant nutrition problems. According to modern ideas, plants utilize the mineral forms of nitrogen, phosphorus, potassium and other elements. In addition, however, the above mentioned investigations indicate that numerous organic compounds (particularly humus substances) activate physiological and biochemical processes in the plant, leading in turn to an increased plant uptake of nutrients from the soil and from applied fertilizers.

It is precisely the multifunctional properties of organic substances which explain the observation that mineral fertilizers are most effective on soil dressed with organic matter. A number of authors have found that it is possible in this way to obtain a good "return" from mineral nitrogen applied to serozems (Belousov, 1955; Ryzhov and Dorman, 1956; Malinkin, 1957); a similar effect was found for sod-podzolic soils (Mamchenkov, 1955, 1957; Nikishkina, 1949).

Timiryazev pointed out that plant physiology provides the theoretical basis for rational agriculture. Therefore in any general scheme for increasing the yields of agricultural crops, the theory of the physiological action of organic substances must be included. This increase may be accomplished both by replenishing the reserve of fresh organic matter in the soil and by using humus fertilizers.

As early as 1936, Dragunov proposed methods for preparing humus fertilizers using peat or brown coal as raw material. When these materials were treated with gaseous ammonia, ammonium humate was formed;

excess ammonia was neutralized with phosphoric acid, and the resulting fertilizer, called humophos, contained up to 14 per cent of P_2O_5 and 9–11 per cent nitrogen, of which 5 per cent is combined with phosphoric acid.

Tests with humophos and ammonium humate (Logvinova and Sannikova, 1936) generally gave positive responses, but they were regarded as basal fertilizers and therefore applied in large amounts. The high cost of preparing humus fertilizers and difficulties in transporting them have restricted their use.

Because humus substances in low concentrations stimulate physiological and biochemical processes in plants, Kristeva has subsequently recommended that humus fertilizers should be applied in small amounts. The methods for preparing these fertilizers were similar in principle to those of Dragunov; the fertilizers were obtained by treating peat and weathered coal with aqueous ammonia solution, subsequently adding superphosphate.

Applied at the rate of 8–10 quintals per hectare to irrigated chestnut soils in the southern Ukraine, these fertilizers increased the yields of maize, wheat, potatoes and various vegetables by 20–30% compared with the unfertilized control.

A number of workers have obtained positive effects by applying humophos to soils in the Ukraine and to degraded chernozems in Siberia. The technology of preparing humophos, the theory of its use and the results obtained from trials with various crops are described in the collection of papers "Humus fertilizers. Theory and practice in their use" (Khristeva, Dragunov *et al.*, 1957).

Niklewski (1960, 1962) has proposed a method, based on the physiological action of humus substances, for preparing peat-humus fertilizers enriched with soluble forms of humus substances. Adding peat-humus fertilizer to farmyard manure considerably increased the yields of many crops.

Growth substances of petroleum origin are regarded as belonging to the group of organic substances which stimulate the development of plants. According to the work of Guseinov (1955, 1958), these substances intensify physiological and biochemical processes and cause changes in the metabolism of the plant.

The humic acid in preparations of humus fertilizers should be in a highly dispersed state, for this favours their penetration into the plant. Humus fertilizers act most effectively when they are in direct contact with the plant root system. Whilst noting the positive action of humus

fertilizers, it must however be remembered that, being added in small amounts, they cannot be regarded as a basal fertilizer; they are only effective when plants are adequately supplied with the major nutrients.

CONCLUSIONS

We have presented data indicating the very important role of organic matter in the life and fertility of soil: (1) in the weathering of rocks and in many decomposition processes of the mineral part of the soil; (2) as a source of nutrients for plants; (3) in the formation of a water-stable soil structure valuable in agriculture; (4) through a direct effect on the plant, promoting, under certain conditions, its growth and development.

We have attempted to show here that these manifold functions are characteristic, not only of strictly humus substances, but also of a large number of diverse organic compounds of an individual nature whose study has so far attracted little attention.

The direct effect of organic substances on the plant is an important problem and has been little studied. The development of investigations in this field is, however, extremely important for understanding the role of organic matter in soil fertility; these investigations are also equally important for establishing principles for the manufacture of organo-mineral fertilizers and for understanding the natural conditions most favourable for their utilization.

CHAPTER 5

THE NATURAL FACTORS OF HUMUS FORMATION

BECAUSE it constitutes a dynamic system, soil humus is subject to continual changes during the processes of new-formation and decomposition of its constituents. The nature of these extremely diverse processes depends on the conditions of soil formation, the plant cover, the activity of micro-organisms and animals, the effect of climate, the chemical, physical and physico-chemical properties of the soil and also on man's activity.

The diverse combination and interaction of these factors determines the state of soil organic matter as indicated by the amount and composition of the humus, its distribution in the profile, the nature of the humus substances and their forms of combination with the mineral part of the soil.

The importance of a study of the relationships existing between the state of soil organic matter and the conditions of soil formation is not in any doubt and has attracted the attention of investigators for a long time.

The problem of the geographical regularities in humus formation was first brought to light by Dokuchaev in his classical work *Russian Chernozem*. His map of the chernozem zone of European Russia showed the distribution of iso-humic belts (i.e. belts with the same humus content in the upper soil layer), indicating that the humus content was highest in central regions of the chernozem zone and gradually decreased in a northerly direction towards podzolic soils, and in a southerly direction towards soils of the dry steppe and semi-desert.

According to Dokuchaev, humus accumulation in chernozems is promoted, in the first place, by perennial grasses and, in the second place, by the particular climatic conditions of the central belt under which the decomposition rate of plant residues is intermediate between the rate in the north and that in the south.

Attempts to show the relationship between the humus content of the soil and the natural conditions of soil formation are also found in Kostychev's works. Kostychev, like Dokuchaev, believed that perennial grasses were favourable for chernozem formation and that the finely branched

root systems of the grasses penetrating the soil in all directions provided, on decay, the best possible source of humus. In this way, Kostychev was able to explain the correlation between the depth of distribution of the humus and the depth of the root systems of grasses, the dependence of the amount of humus on the thickness of the grass cover and also the reason why chernozem formation is not possible under forest.

According to Kostychev, the character of the decomposition of organic matter is of the greatest importance in humus accumulation in the soil. In his opinion, the amount of humus in the soil is determined not by the absolute amount of plant residues added and the amount decomposed, but by the part of the total reserve of organic matter decomposed in unit area during one year. Assuming that the amount of plant residues added and the rate of decomposition of organic matter are constant, every soil has a limiting value for humus accumulation which is reached when the amount of plant residues added is equal to the amount of humus decomposed.

This concept of Kostychev's was developed further by Sibirtsev (1901), who expressed the relationship between the amount of organic matter added, the amount decomposed and the limiting value for humus accumulation by the equation:

$$\frac{1}{n} [(n-1)A + A] = \frac{nA}{n} = A$$

where A = the annual increment of plant residues and n = the denominator of the fraction indicating the degree of humus decomposition. It is evident from this equation that the limit of humus accumulation in the soils is reached when the amount of plant residues added is equal to the amount of humus decomposed.

Later, Tyurin (1937) made this equation more precise by introducing different coefficients for the decomposition rates of plant residues and humus substances, for, as is well known, the latter are decomposed more slowly than fresh plant material. In Tyurin's equation, the rate of accumulation of humus in the soil is determined by the value of the annual supply of organic residues, by their decomposition coefficient and by the humus-decomposition coefficient as follows:

$$S = \left(\frac{1-a}{x} \right) A$$

where S = the limiting value for humus accumulation, a = the decomposition coefficient of plant residues, x = the decomposition coefficient of humus and A = the amount of plant residues added to the soil annually.

It should be borne in mind in examining these equations characterizing the limiting value of humus accumulation in the soil, that they are only applicable when an equilibrium condition is maintained in the soil for a long time. But the very fact that new formation of humus substances is taking place undoubtedly disturbs the equilibrium, as it changes a number of properties and characteristics of the soil (changes in the plant cover, the microbiological activity, soil chemistry and soil structure, etc.). This inevitably affects the amount of plant residues added, their humification rate, the rate of humus decomposition and therefore the limiting value of humus accumulation in the soil.

The complex nature of the relationship between the conditions of soil formation and the accumulation of humus in the soil was pointed out by Kravkov (1906, 1908, 1911). He considered that the humus content of the soil depends not only on the plant cover and the intensity of humification of plant residues, but also on the fixation of humus substances in the soil in the form of organo-mineral compounds.

The relationship between the content and composition of humus and the conditions of soil formation was shown in a number of later works, notably that of Remezov (1933), who carried out systematic investigations on the humus and nitrogen content and humus composition of the main soil groups of the USSR using Waksman's method. Remezov associated differences in the organic-matter content of soils with the history of their origin, and also with the nature of the plant cover and the intensity of humification of the plant residues, which depend on the specific climatic conditions of the soil zone.

Tyurin, in his work on the geographical regularities of humus formation (1949), presented extensive data on the humus and nitrogen reserves, the composition of the humus and the forms of combination between humus substances and the mineral part of the soil for the main soil groups of the USSR. Tyurin also attempted to establish a relationship between the state of soil organic matter and the conditions of soil formation, particularly the hydrothermal factor. We shall return later to an examination of this work.

Some authors have attempted to show the quantitative relationship between the conditions of soil formation and the state of soil organic matter. However, these were only isolated attempts and the regularities established were mostly of an empirical character. Volobuev (1948) developed Tyurin's idea (1937) of a complex interrelationship between the climate (the amount of precipitation and the temperature) and the amount of humus in the soil; he noted that a correlation existed between the humus

reserve and the value of the hydro-factor (Hf) characterizing the change in moisture conditions at different ratios of precipitation (P) and mean annual temperature (T) (Fig. 50). Volobuev calculated the values of the hydro-factor from the following empirical formula:

$$T = 43.2 \log P - Hf$$

where P and T are variables and Hf is a parameter possessing a fixed value for each hydro-series.

For soils with a high humus content the mean Hf values range from 105 to 112; where the humus content is at its highest (deep chernozems)

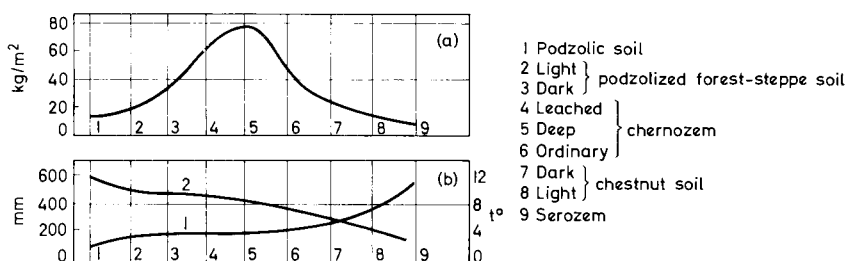


FIG. 50. The humus reserves and climatic conditions of the main soil types and sub-types of the USSR (after Tyurin, 1937).

(a) The humus reserve to a depth of 100—120 cm in kg per m². (b) 1. Mean annual temperature; 2. Mean annual precipitation.

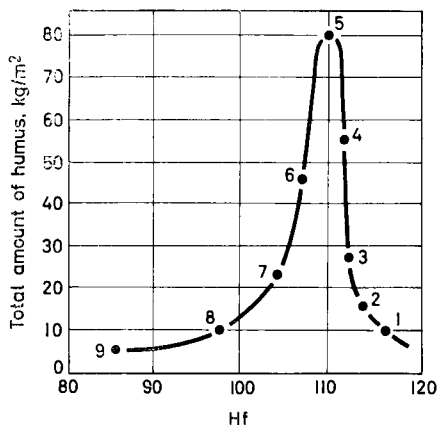


FIG. 51. The variation in the humus reserve of the main soil types and sub-types of the USSR in relation to the hydro-factor. The numbers on the curve correspond to the order of the position of the soils on Fig. 50.

the Hf value is 110. With lower Hf values and, at the other extreme, with values exceeding 112, the humus content decreases sharply (Fig. 51).

Subsequently Volobuev (1958) specified that the index Hf is as a rule related to an index of effective moisture:

$$K_n = \frac{\text{precipitation}}{E_n}$$

where E_n is the natural rate of evaporation. Mean values of Hf (105–110) that are characteristic for soils rich in humus correspond to $K_n = 0.8$ – 1.0 , i.e. to conditions of equilibrium moisture.

From the work of Kostychev, Sibirtsev, Tyurin and Volobuev discussed earlier, it will be seen that the establishment of a mathematical relationship between the conditions of soil formation and humus reserves in the soil is a complex task. In solving it, one should assume, while finding out the importance of one particular factor, that the other conditions of the medium remain constant. Jenny (1941) tried to establish that the nitrogen and humus contents of the soil depends on indexes of annual temperature and moisture factors.

However, being a dynamic system, soil is governed by the dialectic law of development, according to which an alteration in any one factor brings about inevitable changes in the other factors: a change in the temperature (or moisture), for example, inevitably affects the moisture (or temperature) regime of the soil, the nature of the plant cover and the microbiological activity, and therefore the interrelationship between different factors of soil formation is undoubtedly of a more complex character than Jenny indicated in his empirical equations. For this reason these equations are only applicable to soils under similar conditions of formation. Thus, the relationship between the amount of nitrogen and the moisture factor in cultivated steppe soils was expressed by Jenny in the following logarithmic equation:

$$N = 0.320 (1 - e^{-0.0034 NSQ})$$

where N = the total amount of nitrogen in the 0–18 cm layer and NSQ = Meyer's moisture factor.

However, as Jenny pointed out, this equation does not apply to soils occurring under similar climatic conditions, but which were previously under forest.

A similar case was also observed during a determination of the relationship between the amount of humus (and nitrogen) and the temperature. On the basis of Van't Hoff's law on the acceleration of the rate of a

chemical reaction 2–3 times by a temperature increase of 10° C, Jenny proposed the following equation:

$$N = C e^{-kT}$$

where N = the total content of nitrogen or humus in the surface layer of the soil, T = the temperature and C and k are constants.

In accordance with Van't Hoff's law, it was assumed that for every 10° decrease in the annual temperature, the intensity of decomposition of nitrogen or humus decreases 2–3 times and, correspondingly, their content in the soil increases 2–3 times. As Jenny pointed out, however, this equation is only applicable for soils in which the moisture conditions are similar and the plant cover identical. Hence, it does not reflect the broad regularities existing in Nature.

In the following account we shall give data characterizing the importance of the main factors (plant cover, microbiological activity, climate, physico-chemical soil properties) in humus formation. Subsequently, using the main soil groups of the USSR as examples, we shall attempt to show the relationship existing between the conditions of soil formation and the state of the organic matter of these soils.

THE ROLE OF THE PLANT COVER IN HUMUS FORMATION

The participation of the plant cover in humus formation is determined by the amount and nature of the plant residues, their mode of admission into the soil and the nature of their decomposition.

Dokuchaev, Kostȳchev and Williams found that the best source of humus was produced by perennial grasses and legumes which possess finely branched root systems capable of regeneration.

Compared with grass vegetation, the roots of woody species, being thick and long-living, form only small amounts of humus. In forest soils (in the absence of the grass cover) the main source of humus is the litter, and organic matter enters the soil layers in the form of solutions leached from the litter.

Only a small amount of humus is produced by dry steppe vegetation. This is apparent from the statements of Dимо (1907), Keller (1907), Bushinskii (1929) and Williams (1914, 1939) that the distinctive feature of the plant cover of dry steppe is its sparseness and the fact that the majority of the plants (*Artemisia*, *Pyrethrum* and *Kochia*) possess thick root systems.

In the soils first formed on rocks, mosses and lichens are the most important sources of humus.

An important factor determining the humification rate of plant residues is their chemical composition. It is evident, too, from numerous works (reviewed in Chapter 3), that the decomposition rate of plant residues is determined by the ratio between the readily decomposable groups (carbohydrates, proteins) and the difficultly decomposable lignified components, which besides being extremely resistant towards decomposition themselves, also have a retarding effect on the decomposition of tissues situated close to them in the plant.

As already mentioned, the participation of plant residues in humus formation depends on their nature as well as on their mode of admission into the soil. In Table 45 the data of several authors, taken from Tyurin's work (1946) and supplemented to some extent by our data, are given. These data show that there is a relationship between the humus reserve of the soils and the amount of plant residues and their mode of admission into the soil.

The greatest reserve of roots is found in soils of the steppe and forest-steppe zones under forest, where it amounts to 20–27 tons per ha in the 0–27 cm layer. The amount of humus is lower in forest soils than in fallow soil even though the root mass is smaller in the latter—amounting to only 11–12 tons per ha.

The amount of plant residues entering the soil annually is a very important factor in humus formation. It varies widely in different soils, as may be seen in Table 46, compiled from the article by Bazilevich (1962) which summarizes results from his own investigations and from a number of other authors (Mina, 1955; Remezov *et al.*, 1959 — for forest soils; Pershina and Yakovleva, 1960; Rodin, 1961 — for dry steppe soils and deserts).

Under meadow and mixed steppe vegetation, from 65 to 90 per cent of the total plant mass (aerial part and roots) dies, equivalent to 10 tons per hectare or more. Under dry *Artemesia-Stipa-festuca* steppe, and ephemeral *Artemesia* desert vegetation on light serozems, the dying mass amounts to only 6–8 tons per hectare, and under semi-brushwood halophytic desert vegetation on gray-brown soils it does not exceed 1 ton per hectare. In this series of soils, almost the whole plant mass dies each year. Although the total biomass in coniferous and deciduous forests is large, much of it is woody, and the dying green mass and roots amount to only 2–6 tons per hectare.

It should also be considered that secretions from plant roots may take

TABLE 45. CONTENT OF DRY MATTER OF ROOTS AND HUMUS IN SOILS IN TONS PER HECTARE (Tyurin, 1946)

Soil	Vegetation	Horizon (cm)	Humus	Living roots		Dead roots	Author
				total amount	amount of fine roots		
Podzolic loam (Sobakino Exp. Sta., Moscow region)	13-year fallow	0-20	53.2	12.88	10.0	no data	Kachinskii, 1925
	Rye	0-20	53.2	4.41	2.33	no data	
	Oats	0-20	53.2	3.68	3.25	no data	
	Mixed forest	0-12	32.1	18.58	7.00	no data	
Strongly podzolic, heavy loam (Lisino, Leningrad region)	Continuous fallow	0-27	45.7	27.12	7.32	no data	Tyurin, 1935
	Coniferous forest	0-24	85.0	11.0	not determined	not determined	
	Deciduous forest	5-10	16.10	8.8	not determined	not determined	
	Rye	5-25	43.5	12.4	not determined	not determined	
Dark-gray, slightly podzolized degraded clayey chernozem	Deciduous forest	0-15	130.7	15.95	8.14	6.3	Malyanov, 1937
	Rye	0-25	217.4	17.34	9.3	6.76	
	Virgin land	0-10	88.1	3.44	no data	6.96	
	14-year fallow	0-10	101.2	8.54	6.59	2.12	
Fertile loamy chernozem	Virgin land	0-20	202.2	12.73	9.85	3.04	Savvinov and Pankova, 1942
	14-year fallow	0-10	133.2	5.19	5.19	4.03	
	Virgin land (<i>Stipa-Festuca sulcata</i> steppe)	0-25	291.0	8.68	8.68	4.19	
	Virgin land (<i>Festuca sulcata-Artemisi amaritima</i> steppe)	0-15	75.2	3.25	3.25	2.68	
Dark-chestnut, heavy loam (Krasnokutsk Exp. Sta., Saratov region)	Virgin land (<i>Festuca sulcata-Artemisi amaritima</i> steppe)	0-25	113.0	4.55	4.55	3.23	Kononova, 1943
	Residual solonchak-like columnar solonets (Malouzensk Sta., Saratov region)	0-22	71.6	8.79	—	—	
	Light serozem (State Farm, Pakhta-Aral, Kazakh. SSR)	0-10	15.8	20.5	—	—	
	3-year lucerne	0-26	23.0	21.3	—	—	
Dark-chestnut, heavy loam (Krasnokutsk Exp. Sta., Saratov region)	Virgin land	0-26	40.4	12.1	—	—	Kononova, 1943
	3-year lucerne	0-26	40.4	12.1	—	—	

TABLE 46. THE BIOMASS AND DYING COMPONENTS (AERIAL MASS AND ROOTS) IN VARIOUS SOIL-VEGETATION ZONES OF THE USSR

Biocoenoses	Biomass quintals per hectare	As % of biomass		Dying mass (aerial mass and roots)		Nitro- gen in the dying mass %	Nitrogen from dying mass entering soil, kg per hec- tare
		green mass	roots	as % of bio- mass	quin- tals per hectare		
Coniferous forests on sod-podzolic soils	1000-3800	6-2	30-15	1-3	20-64	0.59	11-44
Deciduous forests on gray forest soils	1000-5000	4-2	40-15	1-4	24-64	1.05	25-72
Steppe-like meadows and meadow-like steppes on meadow chernozem soils	115-320	30-35	65-70	50-55	60-80	1.40	90-230
Meadow-like steppes on typical leached chernozems	210-260	20-35	65-80	45-55	100-130	1.20	125-160
Mixed vegetation- <i>Fes- tuca-Stipa</i> steppes on ordinary and southern cher- nozems	180-250	10-20	80-90	40-45	80-110	1.2	90-120
Dry <i>Artemesia-Stipa- Festuca</i> -steppes on chestnut soils	100-230	5-15	85-95	35-45	40-80	1.0	45-70
Ephemeral <i>Artemesia</i> deserts on light serozems	110-140	10-20	80-90	60-85	60-80	1.3	80-110
Semi-brushwood ha- lophytic <i>Artemesia</i> deserts on gray- brown soils	40-50	2-3	85-90	25-30	8-10	1.5	12-18

part in humus formation, although the importance of this is not yet clear. Under sterile culture conditions with changed and unchanged nutrient

media, Meshkov (1961) established that the total organic carbon in the root secretions from maize amounts to about 2.5 per cent and from peas up to 10 per cent of the carbon in the crop mass.

Microbial cytoplasm may also be a source of humus substances in the soil; in the takyr soils, for example, algae are the sole source of organic matter (Bolyshhev, 1952, 1955, 1961). In highly developed soils (podzolic soils, chernozems, serozems), the microbial mass, on a dry matter basis, amounts to no more than 1.2–1.3 tons per hectare and so does not exceed 30 per cent of the total humus reserve (Tyurin, 1946; Mishustin, 1956).

A direct relationship between the humus content and the amount of living and dying plant mass has not been established (see Tables 45 and 46). This is because the humus reserve is determined both by the new-formation and the decomposition of humus substances. In addition, the formation of new humus substances is governed not so much by the total amount of dying plant residues, as by their chemical nature and the character of their transformation by microbial activity.

THE ROLE OF MICRO-ORGANISMS IN SOIL HUMUS FORMATION

There is no doubt that microbial activity is the most important factor in the processes of humus formation. The whole complex of processes by which plant residues are transformed and finally converted into humus is the result of the combined activity of associations of microbes exhibiting diverse biochemical functions.

The fate of the newly formed humus substances—their inclusion in new biological processes and decomposition to final products of mineralization, or their retention in the soil for a certain length of time—depends mainly on the activity of micro-organisms. The humus reserve of the soil is determined by the ratio of the intensity of two processes—the new formation and decomposition of humus substances.

Kostychev's expression:

$$\text{Humus (reserve)} = \text{initial humus (reserve)} + \text{humus (newly formed)} \\ - \text{humus (decomposed)}$$

is not always borne in mind during an analysis of the natural conditions determining the humus reserve of the soil. Thus, Mishustin (1947) related the humus content of the soil to only one set of processes—the new formation of humus substances—and did not take into account the fact that the

humus reserve depends to a similar degree on the second set of processes—their decomposition.

After examining the conditions under which humus formation occurs, Mishustin (1947, pp. 292, 300, 302, 305, etc.) concluded that humus formation in the soil is promoted by a suppression of microbiological activity, in which case only the enzymatic processes of microbial origin maintain their activity.

On the basis of an examination of natural conditions, Mishustin considered that conditions for humus formation are most favourable in chernozems because, in them, periods of summer drought suppress the activity of the microbes and at the same time promote the synthesis of humus substances, a process involving the participation of enzymes of microbial origin, which under these conditions maintain their activity. Thus, Mishustin recognized the existence of a direct relationship between the energy of humus formation (which he considered to be equivalent to the accumulation of humus in the soil) and the suppression of microbiological activity in the soil.

In our opinion, this point needs to be more accurately defined. We fully share Mishustin's view that the synthesis of humus substances occurs under the influence of exo-enzymes produced by micro-organisms. But we cannot share Mishustin's view that enzymes of microbial origin can maintain their activity in the soil for a long period, for after isolation from the bacterial cells, as happens under soil conditions, they undoubtedly become rapidly inactivated. Consequently, the synthesis of humus substances is most active when fresh enzymes are being produced by the living bacteria. In other words, in our opinion, the energy of humus formation is related directly to the activity of the micro-organisms.

There are observed in Nature facts confirming the correctness of our point of view. For example, in considering different varieties of the same type of soil—chernozems—we found that the humus content was highest in those soils (deep chernozems) formed under more favourable moisture conditions, and not in soils formed under a more severe water regime (ordinary chernozems and, particularly, southern chernozems).

Another example contrary to Mishustin's view is the rapid and very great accumulation of humus occurring under perennial grasses (see Chapter 7) in irrigated serozems, which, as is well known, are characterized by very active microbiological activity compared with other groups of soils.

But the principal question arising is: why in this case do serozems have a low humus content? This point, which appears at first to be paradoxical, becomes clear if we turn to the point previously made, that the humus

reserve of the soil is determined not only by the amount of newly formed humus substances but also by the rate of decomposition: in serozems, under conditions of intensive biological activity, both the new formation of humus substances and their participation in new biological processes proceed at a high rate. Therefore, both these sets of processes determining the humus reserve of the soil depend directly on the activity of micro-organisms.

What, in this case, are the most favourable conditions for humus accumulation in the soil? In our opinion, to answer this it is necessary to consider the rhythmical combination of factors producing active microbiological activity (when the new formation of humus substances takes place) and the subsequent depression (inhibiting the decomposition of humus substances). During the periods of depression newly formed humus substances undergo complication, interact with the mineral part of the soil and are therefore less available to micro-organisms during their subsequent periods of increased activity.

These rhythmical conditions are to be found in chernozem soils where the formation of humus substances is associated with periods of moistening (not drying as Mishustin supposed), their conversion into forms less available to microbes being associated with periods of moisture deficiency.

We shall now examine data characterizing the possible microbiological activity in various soils, which can be judged from the number of micro-organisms and their biochemical activity.

Although numerous data on the number of micro-organisms in different soils of the USSR are available, comparison is difficult because of the variety of methods used. We shall not examine the data in detail here but will deal only with the results obtained by investigators who employed the same method for counting the microbes.

The most complete picture of the microbial population of soils is provided by the Vinogradskiĭ method (direct counting under the microscope), of which various modifications were presented. The most important modification was by Germanov (1932), who introduced preliminary treatment of the soil with NaCl to reveal bacteria which the Vinogradskiĭ method failed to detect. As Naumova (1933) showed, the Vinogradskiĭ method gave values that were 7-8 times lower than those obtained with Germanov's modification.

However, since the most reliable data on the number of micro-organisms in different soils of the USSR in the possession of the Institute of Agricultural Microbiology (VASKHNIL) were obtained by the Vinogradskiĭ method, we utilized these data compiled by Lazarev (1939, 1949). These

data are placed with data obtained by other authors using the same method (Table 47).

TABLE 47. NUMBERS OF MICRO-ORGANISMS IN SOILS OF THE USSR
(counted by the Vinogradskiĭ method)

Soils*	Total number of micro-organisms (millions per g soil)	Number of micro-organisms (millions per mg soil nitrogen)	Author
Northern podzol	300-600	—	Kazanskiĭ, 1932
Peat bog	707	51	Lazarev, 1939
Cultivated peat bog	1003	65	Lazarev, 1939
Cultivated podzolic soil	441	153	Lazarev, 1939
Podzolic soil	566	230	Naumova, 1933
Dark-gray forest soil, unmanured fallow	289	102	Naumova, 1933
Ordinary chernozem, old fallow	1930	447	Lazarev, 1939
Southern chernozem, wheat field	3500	1020	Lazarev, 1939
Chernozem, old fallow	2409	630	Lazarev, 1939
Chernozem, arable	2694	730	Lazarev, 1939
Dark chestnut soil, arable	1544	900†	Rikhter, A. A., and V. A., 1925
Serozem, soil of irrigated field	1250	2347	Lazarev, 1939
Serozem, uncultivated, unirrigated	1622	1978	Lazarev, 1939
Irrigated serozem under cotton, unfertilized	1830	2232	Lazarev, 1939
Irrigated serozem under cotton, fertilized with superphosphate	1918	2339	Lazarev, 1939
Serozem	2288	3000†	Stepanova, 1928

* Names of the soils are those given by the authors

† Calculated by us on the basis of the approximate nitrogen content of the indicated soils

Only general conclusions can be drawn from these data, for it is a well-known fact that the number of micro-organisms varies greatly during the course of the year (Rybalkina, 1957; Loub, 1960; and others). Nevertheless, certain points are fairly clear. Thus, the number of micro-organisms increases on passing from peat and podzolic soils to chernozems, and decreases again somewhat in serozem soils. This regularity is observed in both cultivated and uncultivated soils (a new survey of the data on the microflora in soils of the USSR was made by Mishustin, 1956).

Lazarev calculated the number of micro-organisms per mg of soil nitrogen; the data he obtained are indirect criteria of the intensity of mobilization of the soil nitrogen and also, therefore, of the energy of humus decomposition.

It can be seen from the data of Table 47 that on passing from northern peat soils and podzolic soils to chernozems and further to irrigated serozems, the number of micro-organisms per mg of soil nitrogen increases. A similar regularity was noted by Mishustin (1950, 1953, 1956) during a count of the number of microbes per gramme of organic matter.

Systematic investigations on the biodynamics of the major soil types of the USSR were carried out at the Institute of Agricultural Microbiology (VASKHNIL) under the direction of Academician P. A. Kostychev. The results of these investigations, which appeared in several volumes of the proceedings of the Institute (1926–1933), showed that on passing from northern podzols to sod-podzolic soils, chernozems and southern soils (serozems), the population of micro-organisms becomes more diverse, and the mobilization of the nitrogen reserve proceeds at an increasing intensity, reaching a maximum in irrigated serozems.

In this respect the latest data of Soviet microbiologists who have employed eco-geographical principles in their investigations are of particular interest.

Mishustin (1947) showed that on passing from north to south, the living functions of *Bac. mycoides* change: the optimum temperature, the rate of multiplication and the enzymatic activity increase. Sushkina (1949) found a relationship between the occurrence of *Azotobacter* and factors of soil formation—the plant cover, some physico-chemical properties and the moisture regime—in soils of the USSR.

For judging the role of micro-organisms in the transformation of organic matter in soils, the investigations of Rȳbalkina (1951, 1952, 1957) who studied groups of putrefying bacteria, the anaerobic nitrogen fixer *Clostridium Pasteurianum* and groups of micro-organisms decomposing cellulose, are interesting and important. Rȳbalkina found that in podzolic-gley and humus-ferruginous soils of the north these groups of bacteria show very little activity and require supplementary substances (yeast autolysates, etc.) for their growth. On passing towards the south, the soils become more densely populated by micro-organisms, their composition becomes more diverse and their biochemical functions more active; soil improvement considerably increases the activity of the micro-organisms.

During studies of the group of cellulose-decomposing micro-organisms Rȳbalkina also found that in dwarf-podzols and surface-gleyed soils of

the north, cellulose decomposition is brought about by fungi and actinomycetes. Cellulose myxobacteria (*Cytophaga Hutchinsonii*) are physiologically weak and develop very slowly. In sod-podzolic soils, cellulose decomposition proceeds much more actively, under deciduous forests and in cultivated soils in particular, and less actively under coniferous forests. In these soils the myxobacteria group is predominant and diverse in composition (*Cytophaga*, *Cellvibrio*, *Polyangium*, *Angiococcus*), fungi and actinomycetes occupying a secondary position. In deep chernozems cellulose decomposition proceeds in much the same way as in sod-podzolic soils.

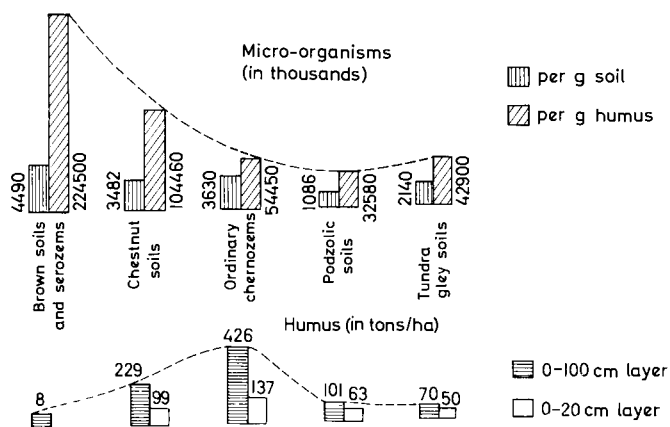


FIG. 52. Micro-organisms and humus in soils of the USSR.

From available data on the quantitative determination of micro-organisms, their group composition, biodynamics and the biochemical activity of individual representatives, it can be concluded fairly confidently that the microbiological activity of the soil increases on passing from northern podzols to sod-podzolic and gray forest soils, increases further on passing towards chernozems and is highest in serozems.

A comparison of data on the numbers of micro-organisms (from Mishustin, 1956) and the humus reserves of the major soil types of the USSR is given in Fig. 52. This shows that the soils richest in humus are characterized by moderate numbers of micro-organisms. Consequently, it can be assumed that moderate microbiological activity is favourable for the accumulation of humus in soils (regarding the accumulation as the difference between the new formation and the decomposition of humus substances).

In examining these data, it should be borne in mind that they reflect the potential microbiological activity, which is possible only under defined conditions of temperature and soil moisture. We shall now examine data characterizing the hydrothermal conditions of different soils.

THE INFLUENCE OF HYDROTHERMAL CONDITIONS ON HUMUS FORMATION

Data on the intensity of microbiological activity in relation to the hydrothermal factor, i.e. to a combination of temperature and moisture, are extremely scanty.

The difficulty with these investigations is that the various groups of micro-organisms, which participate to varying degrees in the transformation processes of organic matter, exhibit different temperature and soil-moisture requirements. Furthermore, in different soils even the same systematic groups of bacteria show adaptations to the temperature conditions (Mishustin, 1925, 1947). Hence, the problem of the effect of temperature and moisture on the intensity of microbiological activity in soils should be solved at the present in general terms, on the assumption that the most active role in the transformation of organic substances belongs to mesophilic micro-organisms.

It is usual to regard the relationship between microbiological activity and temperature as conforming to Van't Hoff's law for monomolecular chemical reactions. According to this law, the velocity of a reaction is doubled or trebled by a temperature increase of 10° C; accordingly, it has the form of an exponential curve conforming to the equation:

$$V = Ca^t$$

where V = the velocity, C = the temperature, a = a certain coefficient near to unity, and t = the coefficient of temperature increase.

However, some works mention that deviations from this law are to be found in biological processes, namely, at low temperatures the temperature coefficient Q_{10} is greater than 2–3; at high temperatures it is smaller. For instance, Lehenbauer (1914), determining the growth of maize seedlings at different temperatures found that over the range 0–10° C the coefficient of growth intensity was 10; at 30° it was unity and only within the range 20°–30° did it have a value of 2–3, conforming to Van't Hoff's law.

A further increase of temperature above 35° suppressed plant growth and therefore reduced the coefficient of growth intensity (temperature coefficient Q_{10}) to less than unity (Table 48).

TABLE 48. GROWTH OF MAIZE SEEDLINGS AT DIFFERENT TEMPERATURES
(Lehenbauer, 1914)

Indices	Temperature (°C)								
	12-22	13-23	15-25	18-28	20-30	21-31	22-32	25-35	32-42
Growth in 0.01 mm	9-59	10-64	20-75	28-98	45-108	53-109	59-111	75-86	111-11
Temperature coefficient, Q_{10}	6.56	6.40	3.75	3.50	2.40	2.60	1.88	1.15	0.09

In microbiological processes (multiplication, respiration, enzymatic activity of microbes) a similar deviation from Van't Hoff's law is also detected; the value of the temperature coefficient remains constant or changes only slightly within a relatively narrow temperature range—a value of 2–3 for the coefficient Q_{10} is only observed within the range 15–20° C. At higher temperatures the coefficient decreases and at low temperatures it increases (Imshenetskiĭ, 1944). Similar instances appear in works which deal directly with the transformation processes of organic matter in the soil.

In works on the decomposition of organic matter at different temperatures, the intensity of the process was calculated from the amount of CO₂ evolved (Müller, 1887; Dehérain and Demoussy, 1896; Fodor, 1875; Wollny, 1886; Kostȳchev, 1886). These works indicate that a slight decomposition of organic matter beings even at 0°; the intensity of the process increases considerably with a temperature increase of up to 35°, but above this temperature a suppression of the process takes place. However, with a further increase in temperature above 50° C an increased evolution of CO₂ is again observed, which appears to be due entirely to chemical processes of organic-matter decomposition; in Nature these occur only in the moist surface layers of soil in a hot climate.

In Table 49 the results of Wollny's experiments are given. The optimum temperature in these experiments was 40° C. From a calculation of the value of the temperature coefficient Q_{10} at different temperature ranges we also found that its value, as a rule, decreased with increasing temperature.

We shall examine now the works of Waksman and Gerretsen (1931), who investigated the decomposition rate of straw at various temperatures and with optimum moisture contents of 66 and 80 per cent. They based their results on the loss of weight of the straw.

TABLE 49. EFFECT OF TEMPERATURE ON DECOMPOSITION OF ORGANIC MATTER.
CONTENT OF CO₂ IN mg PER LITRE OF SOIL AIR (Wollny, 1886)

Moisture	Temperature (°C)				
	10	20	30	40	50
At moisture 26.79 %	18.38	54.24	63.50	80.06	81.52
Value of Q_{10}	2.9	1.15	1.26	1.02	
At moisture 46.79 %	35.07	61.49	82.12	91.86	97.48
Value of Q_{10}	1.75	1.33	1.12	1.06	

Their experiments show the general pattern of the increase in the intensity of straw decomposition with a temperature rise (7° to 37° C). From their results we calculated the value of the temperature coefficient Q_{10} . Here also it was found that the value of the coefficient decreased with increasing temperature (Table 50). Thus, within the temperature range 7–18° C, the temperature coefficient was 2.3–1.62, between 18–27° C it was 1.16–1.15 and between 27–37° C it was only 1.09.

TABLE 50. RATE OF STRAW DECOMPOSITION IN THE EXPERIMENTS OF WAKSMAN AND GERRETSEN (1931). VARIANT WITH MINERAL FERTILIZERS

Temperature (°C)	Amount decomposed as % of the original amount				Temperature coefficient at 80 % moisture	
	at 66 % moisture		at 80 % moisture			
	during 105 days	during 273 days	during 105 days	during 273 days	during 105 days	during 273 days
7	27.3	35.7	23.2	36.3	—	—
18	46.8	50.5	53.3	60.8	2.3	1.62
27	55.9	64.7	62.4	70.1	1.16	1.15
37	60.2	70.0	68.0	76.4	1.09	1.09

From an examination of works on the effect of temperature on the activity of micro-organisms participating in the transformation of organic substances, the following conclusions can be drawn:

1. The activity of microbes increases with increasing temperature from 0 to 35° C; 35° C can be regarded as the optimum value because a further increase in temperature has a suppressing effect.

2. Van't Hoff's law, applied to microbiological processes, needs further precision with regard to the value of the temperature coefficient at different temperature ranges. The greatest "flush" in the intensity of these processes

with increasing temperature can be expected within the low temperature range; as the optimum temperature is approached the value of the coefficient decreases.

With regard to the effect of moisture on the activity of micro-organisms taking part in the transformation of organic matter the following indications can be found in the literature.

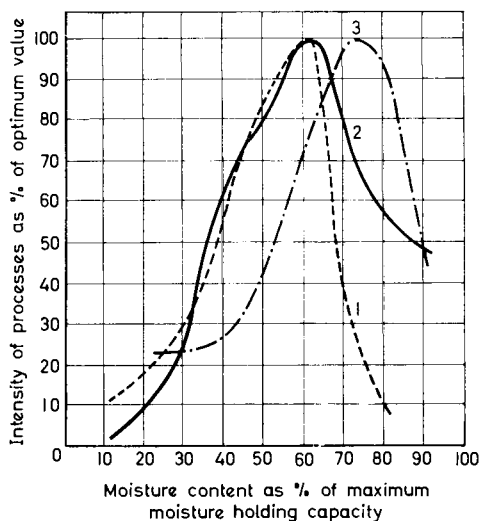


FIG. 53. The intensity of biological processes at various soil-moisture levels (from the work of Greaves and Carter, 1920) 1. Nitrification; 2. Ammonification; 3. Nitrogen fixation.

Micro-organisms show some degree of activity at extremely low moisture levels; fungi, actinomycetes and a number of bacteria, for instance, begin to grow even at a moisture level corresponding to maximum hygroscopic moisture (Novogrudskii, 1946, 1947; Enikeeva, 1948). However, the optimum moisture level for the majority of soil micro-organisms is 60–80 per cent of maximum water-holding capacity. Greaves and Carter (1920) carried out a number of laboratory experiments to determine the intensity of nitrification, ammonification and nitrogen assimilation at various levels of soil moisture. The experiments were carried out with 22 soils differing in mechanical composition and humus content.

It was found that for the first two processes the optimum moisture was 60 per cent, and for nitrogen assimilation it was 70–80 per cent of maximum water-holding capacity. An illustration of the intensity of accumulation of NO_3 and NH_3 and the amount of assimilated nitrogen as values relative to the optimum indices is given in Fig. 53.

Detailed investigations on the intensity of decomposition of plant residues and humus at different moisture levels were carried out by Wollny and by Kostychev. These investigations are of particular interest because various combinations of moisture and temperature were used. From the results of these works we have drawn curves (Figs. 54, 55, 56) on the basis of which we consider the following generalizations can be made:

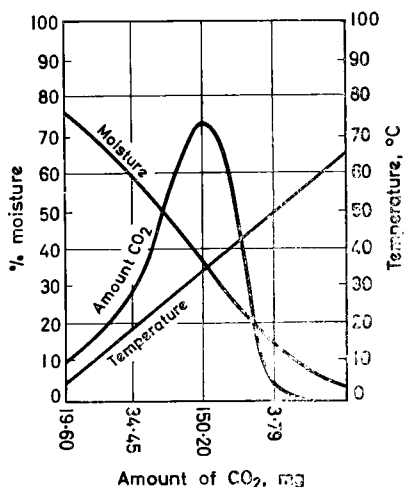


FIG. 54. The intensity of organic-matter decomposition at various combinations of temperature and moisture (from the data of Kostychev, 1886).

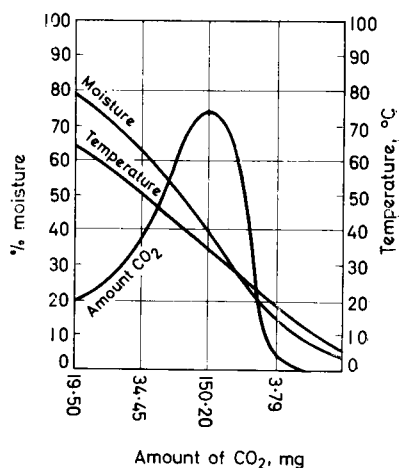


FIG. 55. The intensity of organic-matter decomposition at various combinations of temperature and moisture (from the data of Kostychev, 1886).

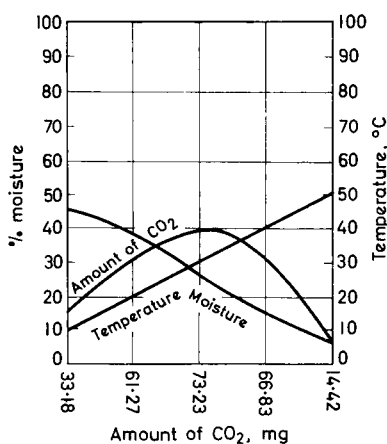


FIG. 56. The intensity of organic-matter decomposition at various combinations of temperature and moisture (from the data of Wollny, 1886).

1. The greatest intensity of decomposition of organic matter, calculated from the amount of CO_2 in the soil air, is observed at moderate temperature values (about 30°C) and with a moisture level of about 30 per cent of the soil weight, corresponding approximately to 60–80 per cent of the maximum moisture-holding capacity.

2. A simultaneous increase of temperature and moisture or their simultaneous decrease in relation to the optimum value decreases the intensity of organic-matter decomposition.

3. With increasing value of one of the two indicated factors and simultaneous decrease of the other, the intensity of decomposition of organic matter—as with any biological phenomenon—is governed by the limiting factor.

Furthermore, with the accumulation of more experimental data, it may be possible to reveal the mathematical character of the relationship existing between the decomposition rate of organic matter and the hydrothermal factor. An attempt of this sort was made by Feher and Frank (1937). Measuring the intensity of microbial activity by determining the number of bacteria and the changes in pH of the medium, he assumed that the activity of micro-organisms depends on the factor R , whose value is expressed by the empirical equation:

$$R = \text{moisture} \times [T^\circ + 10]$$

In our investigations characterizing the possible intensity of organic-matter decomposition in relation to the hydrothermal factor we utilized temperature data from meteorological records, and for characterizing the moisture regime we used moisture coefficients provided by Ivanov (1948). These coefficients represent the ratio of the amount of precipitation to the evaporability (i.e. the amount of evaporation under the prevailing conditions of temperature and air humidity at the place of the investigation).

Ivanov quotes the following values of the moisture coefficient for different zones:

K

1.5	zone of excess moisture (moist forests)
1.49–1.0	zone of sufficient moisture (forest of sufficient moisture)
0.99–0.60	zone of moderate moisture (forest steppe)
0.59–0.30	zone of insufficient moisture (steppe)
0.29–0.13	zone of scanty moisture (semi-desert)
0.12–0.00	zone of negligible moisture.

In considering the results of the experiments on the effect of various combinations of temperature and moisture on the intensity of biological processes we adopted the following scale for the conditions which interested us most:

Soil temperature (°C)	Moisture coefficient	Possible intensity of microbiological activity
> 30	> 1.5	weak
30–20	1.49–1.0	very intensive
20–10	0.99–0.60	fairly intensive
10–5	0.59–0.30	weak
< 5	0.29–0.13	very weak

We used this scale for compiling schemes of the possible seasonal intensity of biological activity in various soil types (see Chapter 6).

It should be noted that Thornthwaite (1948), for particular locations in the USA, and Volobuev (1959), for a number of soils in Europe, Asia and America, have used the principle of constructing plots of the annual cycle in the potential evaporation of precipitation and the deficiency or excess of moisture.

The moisture conditions of the soil medium, apart from their effect on the intensity of microbial activity, play a great role in the mechanism of formation of the molecules of humus substances (this problem was mentioned in the section dealing with humus substances as a system of high-molecular-weight compounds—Chapter 2).

The size of the molecule of humus substance, as in the case of any high-molecular-weight compound, depends on the conditions of the medium, in particular, on the rate at which condensation by-products (water) preventing the growth of the molecule are removed. Accordingly, the soil conditions in the zone of excessive moisture (podzolic soils, krasnozems) favour the formation of humus substances with a smaller size of molecule than the conditions in soils characterized by a periodic moisture deficit (chernozems), where the removal of condensation by-products is ensured.

Corresponding data on the importance of the hydrothermal factor in humus formation for the main soil groups of the USSR are discussed below.

THE INFLUENCE OF CHEMICAL AND PHYSICO-CHEMICAL SOIL PROPERTIES ON HUMUS FORMATION

The diverse role of the chemical and physico-chemical properties of the soil in processes of humus formation are attributable on the one hand to their effect on microbiological processes and hence on the processes of new-formation and decomposition of organic matter. On the other hand, there can be no doubt about the important role of the chemical and physicochemical properties of the soil in the fixation of humus substances in various forms of organo-mineral compounds and therefore in their retention in the soil.

An important part in the process of humus formation is played by lime—a fact noted by many investigators. The previously disputed question as to whether lime stimulates or retards the decomposition of organic matter can now be regarded as fairly clear. The laboratory investigations of numerous workers as well as observations in Nature have indicated that lime (and exchangeable Ca^{2+}) has a two-fold importance in humus formation.

Numerous investigations by various workers¹ have demonstrated the stimulating effect of lime on the decomposition of fresh plant residues; this, apparently, is associated mainly with an increase in soil pH (Table 51)

TABLE 51. INTENSITY OF DECOMPOSITION OF ORGANIC MATTER IN THE SOIL AT VARIOUS RATIOS OF Ca^{2+} AND H^+ . AMOUNT OF CO_2 EVOLVED IN mg PER 100 g SOIL + 0.75 g OF PLANT RESIDUES (Kononova, 1937)

Duration of the investigation	Slightly podzolic soil*				Ordinary chernozem*			
	3·8	5·2	7·1	8·4	3·8	5·8	6·8	8·4
After 1st month	430·6	622·0	834·9	909·3	339·0	602·2	838·1	1042·9
After 2nd month	252·8	417·6	346·7	299·6	169·4	279·6	237·6	267·6
After 3rd month	140·6	144·6	107·0	117·0	100·4	111·6	106·2	103·6
Total	824·0	1184·2	1288·6	1325·9	608·8	993·4	1181·9	1414·1

* Samples for the experiment were prepared by means of the partial replacement of exchangeable Ca^{2+} and H^+ (the experimental method is given in Kononova's work, 1937).

¹ For a review of the literature see works of Rode (1927); Tyulin (1926); Chizhevskii (1932–1933); Kononova (1937); Tyurin (1937).

At the same time, the results of a number of investigations have shown that lime (and exchangeable Ca^{2+}) retards the decomposition of humus substances because of the formation of Ca-humates and organo-mineral compounds less available to micro-organisms. Kostychev had already concluded from his experiments that lime intensifies the disintegration of fresh plant residues but retards decomposition during the later stages of humification. The natural formation of soils with a high humus content on parent rocks rich in alkaline-earth bases in the steppe zone (chernozems) and in the zone of podzolic soils (rendzinas) is direct evidence that an accumulation of humus substances is possible in the presence of lime (and exchangeable Ca^{2+}).

However, soils rich in lime do not always have a high humus content; there are, for example, serozems with a lime content of 15 per cent or more which are poor in humus. The reason for this apparent inconsistency is the high level of biological activity in serozems, which brings about the decomposition and mineralization of humus substances as well as of fresh organic residues.

Turning to the importance of exchangeable sodium in the processes of humus formation, the works of Chizhevskii (1933) and Kononova (1940) indicate that small amounts of sodium increase the intensity of decomposition of organic matter; this can be explained by the increased pH, by the partial conversion of humus substances into a more dispersed form (more available to microbes) and also, possibly, by the desorption of micro-organisms previously present in the soil in an absorbed state.

However, with large amounts of exchangeable sodium (corresponding to its level in solonets) microbiological activity is suppressed as a result of the deterioration of physical properties, in particular, aeration.

TABLE 52. THE INTENSITY OF DECOMPOSITION OF SOIL ORGANIC MATTER AT VARIOUS $\text{Ca}^{2+}/\text{Na}^{+}$ RATIOS. THE AMOUNT OF CO_2 EVOLVED IN mg PER 100 g SOIL + 0.75 g OF PLANT RESIDUES (Kononova, 1940)

Duration of the investigation	Ca^{2+} — 58.3 m eq Na^{+} — none pH — 7.40	Ca^{2+} — 50.3 m eq Na^{+} — 6.0 m eq pH — 7.86	Ca^{2+} — 44.3 m eq Na^{+} — 14.0 m eq pH — 8.22
After 1st month	1268.2	1252.4	1238.1
After 2nd month	295.2	538.9	627.7
After 3rd month	96.9	254.5	233.7
Total	1660.3	2045.8	2099.5

Data from our experiments on the intensity of decomposition of organic matter in the soil at various $\text{Ca}^{2+}/\text{Na}^{+}$ ratios are given in Table 52. The soil samples were prepared by means of the partial replacement of the exchangeable calcium in the soil by sodium.

The problems concerning the role of other mineral compounds of the soil in the processes of humus formation, particularly in the decomposition of organic matter, have been little studied. There are indications (Kinzerskaya, 1935) that these processes are retarded when sulphates of iron and aluminium are present in the soil. Ponomareva (1940) showed that a small amount of manganese sulphate acts as a catalyst, increasing the energy of humus oxidation. In her opinion, MnSO_4 at 50 kg per ha can be used as a fertilizer on deep humic soils.

The capacity of the soil for fixing organic substances depends on its physico-chemical properties. This point attracted the attention of investigators as early as the last century and it became the subject of intensive study in connexion with discussions on the possible movement of organic substances in the soil (Zalomanov, 1879; Barakov, 1886; Kostȳchev, 1884, 1889; Levakovskii, 1888).

Important investigations on the problem of the fixation of organic substances in the soil were carried out by Kravkov (1911, 1938) and his school (Shilova, 1939, 1945; Simakov, 1938, 1951, 1954). They demonstrated that this phenomenon is of complex character, depending on the nature of the substances on the one hand and on the chemical and physico-chemical properties of the soil on the other. Clay, in particular, promotes the adsorption of organic substances in the soil; therefore, mixing the latter with soils of light mechanical composition is a means of fixing the humus. The fact that during adsorption the properties of substances change (Lindau and Rhodius, 1935) and the substances become less available to micro-organisms is of great significance in the adsorption of organic substances and in their retention in the soil.

In Chapter 4 (section "Role of organic matter in the formation of soil profiles; forms of linkage between soil organic matter and the mineral part of the soil") we dealt with the interaction of humus substances with clay minerals. There are indications that during this interaction, humus substances become less available to micro-organisms. Sen (1961) observed such a phenomena during the decomposition of humic acid mixed with montmorillonite or illite; the former mineral, particularly in the presence of Al^{3+} , was more inhibiting than illite.

A number of authors have shown that not only humus substances but also compounds of an individual nature, such as proteins, organo-phosphorus

compounds, cellulose, hemicelluloses and other substances, strongly interact with clay minerals, thereby becoming less available to micro-organisms.

The work of Demolon and Barbier (1929), Mattson (1932) and Ensminger and Giesecking (1939, 1941) indicates that proteins sorbed by clay minerals become resistant to decomposition. The latter authors showed (1942) that albumin and haemoglobin sorbed by kaolin are freely attacked by the proteolytic enzymes pepsin and pancreatin, whereas when linked to montmorillonite, 50–70 per cent remains unattacked by the enzymes. Similar phenomena have been observed by other authors (McLaren, 1954, 1958, 1959; Esterman *et al.* 1959; Pinck, Allison *et al.*, 1951b, 1961). It was shown that proteins sorbed by clay minerals are held not only by van der Waals' forces but also by ionic exchange with inorganic cations, that is, by reaction between the basic groups of a protein molecule and the acid groups of a clay.

Nucleic substances can also be sorbed by minerals, particularly by montmorillonite and, to a lesser degree, by illite and kaolinite (Goring and Bartholomew, 1950, 1951, 1952; Mortland and Giesecking, 1952; Flaig, Kuron and Kaul, 1955). Nucleic substances bound to clay minerals are less easily dephosphorylated by nucleases (Bower, 1949). There are indications that nucleic substances accumulate in soils in combination with iron and aluminium (Mattson and Koutler-Andersson, 1947; Bower, 1949—see Bremner, 1951).

There is evidence showing that clay minerals can sorb carbohydrates. Thus montmorillonite forms complexes with one or two sugar molecules in the interlamellar space of the mineral (Greenland, 1956). Kaolinite and montmorillonite can sorb cellulose, hemicelluloses and their derivatives (Lynch, Wright and Cotnoir, 1956, 1957). At the same time it was noted that the high-molecular-weight derivatives of cellulose (methyl cellulose, hydroxycellulose) were less strongly sorbed than the derivatives of lower molecular weight.

Thus the sorption by minerals, particularly clays, of humus substances and organic compounds of an individual nature (proteins, organo-phosphorus compounds, carbohydrates) favours their preservation and gradual incorporation into the biological cycle. This aspect is undoubtedly of practical importance for soils of light mechanical composition; by applications of clay it is possible to retard the decomposition of humus and protect it from rapid mineralization, which is usually accompanied by an unproductive consumption of nutrients in the humus. Experiments by Simakov (1954) have shown the effectiveness of clay applications to sod-podzolic soils of light mechanical composition.

The direct relationship between the amount of mineral colloid fraction in the soil, with high exchange capacity and the humus content is a consequence of the sorption of organic substances by the clay minerals causing a limitation of their availability to micro-organisms. The data in Table 53 show that on passing from podzolic soils to rich chernozems the exchange capacity of the mineral part of the soil and the humus content both increase, whereas from southern chernozem to chestnut soils and serozems, exchange capacity and humus content both decrease.

The existence of a relationship of this type makes it possible to extend and make more precise our ideas on the factors promoting the accumulation of differing amounts of humus in different soils.

TABLE 53. THE RATIO BETWEEN THE EXCHANGE CAPACITY AND HUMUS CONTENT IN SOILS OF THE USSR (from the data of Vinokurov, Madanov and other authors, see Gorbunov, 1948)

Soil	Horizon	Humus determined by Tyurin's method	Exchange capacity (m eq per 100 g soil)		Ratio between exchange capacity and humus content	
			mineral part*	organic and mineral part	mineral part	organic part
Strongly podzolic	A_p †	2.82	7.22	10.08	71	29
	A_2	0.66	5.24	6.16	90	10
Moderately podzolic	A_p	3.24	7.07	12.56	56	44
	A_1	2.74	6.74	12.02	56	44
Slightly podzolic	A_p	5.29	14.65	26.54	55	45
	A_1	5.34	15.07	23.09	65	35
Slightly podzolic, dark-gray	A_p	6.13	13.69	35.29	39	61
	A_3	4.97	15.46	34.09	45	55
Degraded chernozem	A_p	8.02	20.16	48.35	42	58
	A_1	5.50	23.24	47.88	48	52
Rich chernozem	A_p	11.10	23.82	62.64	38	62
	A_1	11.30	23.53	63.98	37	63
Ordinary chernozem	A_p	7.90	25.68	56.86	45	55
	A_1	5.96	25.00	52.91	47	53
Southern chernozem	A_p	4.95	24.66	42.50	58	42
Chestnut soil	A	2.07	8.60	16.68	65	35
Serozem	A	1.93	6.89	13.15	52	48

* The determination of the exchange capacity of the mineral fraction of the soil was carried out after the oxidation of organic matter with H_2O_2 .

† A_p = ploughed layer.

For instance, it becomes clear that the low humus content of serozems is attributable not only to the high rate of decomposition of organic matter but also to the fact that because of their low absorption capacity, the fixation of humus substances in the form of organo-mineral compounds is negligible. The accumulation of large amounts of humus in chernozems depends to a considerable degree on the high exchange capacity of these soils.

CONCLUSIONS

From this account it follows that each of the examined factors of soil formation — plant cover, the activity of the micro-organisms, hydrothermal conditions, chemical and physico-chemical properties of the soil — is of importance in the transformation of organic substances in the soil and in the long run determines the state of the organic matter.

In the following chapter we shall attempt, using the data available, to characterize the state of the organic part of various soils in relation to the natural conditions of their formation.

CHAPTER 6

CHARACTERISTICS OF THE ORGANIC MATTER IN THE MAIN SOIL TYPES OF THE USSR

MAIN PRINCIPLES GOVERNING HUMUS FORMATION

THE NATURE of humus and the causal relationship between the state of humus and the conditions of soil formation have been intensively investigated by research workers in Russia during the pre-Revolutionary period and particularly since the Soviet era.

Dokuchaev's theory that changes in the amount of humus in various soils were zonal in character was developed by Dokuchaev's and Sibirtsev's followers, who were able to show in addition that certain qualitative differences reflected in varying degrees the mobility of humus (Kozlovskii, Lesnevskii, Shcheglov, Naletov and others—see Tyurin, 1949).

By the first decades of the present century, detailed studies had been made of the humus and nitrogen contents and the carbon-nitrogen ratios of soils. Classified data from that period can be found, for instance, in Kossovich's (1916) textbook on soil science.

Since the Revolution, investigations on soil humus have been widened and have taken on a more fundamental character. Many soil scientists have substantially supplemented the data on the carbon and nitrogen contents of soils of the USSR; this work has been surveyed by Remezov (1933), Tyurin (1937, 1949) and Bolotina (1947). The humus and nitrogen contents of Siberian soils have been classified by Gorshenin (1935). Data for Central Asia have been collected by a group of soil scientists (Bogdanovich *et al.*, 1949) and by Rozanov (1951). For Azerbaidzhan a general survey was made by Volobuev (1950) and Aliev (1956), and for Georgia by Sabashvili (1948).

Great initiative in the study of the state of humus in soils and in the clarification of the geographical principles governing humus formation was taken by Tyurin, who developed a number of methods for this purpose. Tyurin's data, now supplemented by many Soviet soil scientists, make it possible to outline the regular changes in the percentages of humus and

nitrogen, in their total reserves, in the C:N ratio and in the composition of humus for the main soils of the USSR. Figure 57 and Tables 54 and 55 have been compiled from the data of Tyurin, with supplementary material from work published more recently (for a review of this work, see the paper by Kononova, *Pochvovedenie*, No. 11, 1957; and the book by the same author, *Soil Organic Matter*, Acad. Sci. USSR, Moscow, 1963, in Russian).

Humus and nitrogen reserves: C:N ratio

1. In soils of the chernozem series, the highest content of humus and nitrogen occurs in deep (fertile) chernozems.

2. Towards the north and south the humus and nitrogen reserves of these soils gradually decrease, the decrease being more rapid towards the south.

3. From a comparison of the humus and nitrogen reserves of the 0–20 cm and 0–100 cm layers, fundamental differences can be seen in the nature of the humus distribution in various soils. In the soils of forest regions, approximately 50 per cent of the total humus content of the 0–100 cm layer is concentrated in the top 20 cm; below 20 cm the humus content decreases rapidly with increasing depth.

In the soils of steppe regions—chernozems—there is a more gradual decrease in the humus content with increasing depth, only 24–32 per cent of the total humus content of the 0–100 cm layer occurring in the top 20 cm. Lastly, in the soils of drier regions—in chestnut soils and particularly in serozems—the humus concentration in the top layer is once again rather higher than it is in chernozems, the amount in the top 20 cm being 43–45 per cent of the total content in the 0–100 cm layer.

Characteristic carbon/nitrogen ratios are found in the soils of the USSR; within the series ranging from northern podzolic soils to chernozems and further to serozems, the widest C:N ratios (> 10) are observed in the top 20 cm of chernozems and dark chestnut soils. In the gray podzolized soils of forest steppe and podzolic soils of the northern forest zone (except in virgin, deep-humic soils) the ratio decreases to 10.5–9.7.

The narrowest C:N ratio (approximately 8) is observed in serozems; in these soils the humus is richer in nitrogen than it is in chernozems and podzolic soils.

The soils of the humid sub-tropics (krasnozems) are unique; they contain a large amount of humus, over 50 per cent of which occurs in the top 20 cm. Typically, the humus of krasnozems contains very little

TABLE 54. THE RESERVE OF HUMUS AND NITROGEN IN SOILS OF THE USSR IN TONS PER HECTARE (Tyurin, 1949)

Soil	Humus		Nitrogen		C:N ratio in 0-20 cm layer
	in 0-100 cm layer	in 0-20 cm layer	in 0-100 cm layer	in 0-20 cm layer	
Strongly podzolic	101	63	6.6	3.3	10.8
Medium podzolic	94	50	6.1	3.2	9.0
Slightly podzolic	104	54	7.2	3.1	10.1
Podzolic (average)	99	$\frac{53}{54^*}$	6.6	3.2	9.7
Gray, slightly podzolized	175	—	9.4	5.6	10.7
Dark-gray, slightly podzolized	296	—	14.0	6.6	10.3
Forest steppe, podzolized (average)	215	$\frac{109}{51}$	12.0	6.0	10.5
Degraded chernozems	452	132	25.2	7.0	11.0
Leached chernozems	549	192	26.5	9.4	11.8
Degraded and leached chernozems (average)	512	$\frac{164}{32}$	—	—	—
Deep chernozems	709	$\frac{224}{32}$	35.8	11.3	11.5
Ordinary chernozems	426	$\frac{137}{32}$	24.0	7.0	11.3
Southern chernozems	391	$\frac{93}{24}$	17.0	6.3	8.6
Dark chestnut	229	$\frac{99}{43}$	13.2 (for 0-50 cm layer)	5.6	11.2
Chestnut and light chestnut	156	—	—	—	—
Dark serozems	128	—	11.8	3.8	8.2
Typical serozems	83	—	7.5	2.5	8.4
Light serozems	67	—	6.4	2.3	7.8
Serozems (average)	83	$\frac{37}{45}$	—	—	—
Krasnozems	282	$\frac{153}{54}$	10.5	4.7	18.9

* Denominator indicates the amount of humus in the top 20 cm as a percentage of the total amount in the 0-100 cm layer.

nitrogen, as a result of which the C:N ratio is very wide—18.9 (Table 54 and Fig. 57).

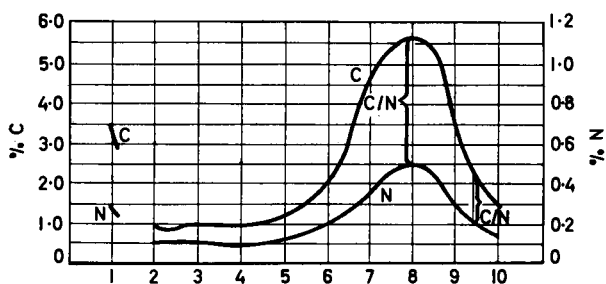


FIG. 57. Percentage of carbon and nitrogen in soils of the USSR; C : N ratio. 1. Krasnozems; 2. Light serozems; 3. Typical serozems; 4. Brown steppe soils; 5. Light chestnut soils; 6. Dark chestnut soils; 7. Ordinary chernozems; 8. Deep chernozems; 9. Gray forest soils; 10. Podzolic soils.

The composition of humus in soils

From investigations on the humus composition of almost all the main soil types, carried out for the most part by Tyurin and his co-workers, the following regularities can be stated:

1. Most characteristic of soil humus is the group of humic acids whose content changes regularly with changes in the total humus content. Tyurin believed, therefore, that natural conditions favouring the accumulation of humic acids are at the same time favourable for humus accumulation. The relative content of humic acids in the humus increases on passing from podzolic soils to chernozems but then decreases through chestnut and brown soils of the desert steppe to serozems.

2. Changes in the fulvic-acid¹ content are less regular, but generally an inverse relationship exists between the fulvic-acid and humic-acid content. The ratio of the content of humic acids to fulvic acids is very characteristic. In chernozems and dark chestnut soils this ratio approaches unity and in individual cases may exceed it. In podzolic soils and serozems, however, the fulvic-acid content is greater than the humic-acid content by 2–3 times or more.

3. The composition of humus of krasnozems is unique. Fulvic acids are predominant, amounting to 50 per cent of the total humus content, while the amount of humic acids is only 15 per cent (Table 55).

¹ In Tyurin's scheme for determining humus composition, fulvic acids represent the sum of the organic substances of the acid solution after precipitating humic acids from the alkali extract.

TABLE 55. COMPOSITION OF HUMUS IN SOIL OF THE USSR (for the Upper Humus Horizon)

Soil	Humus content %	Carbon of main groups, as % of its total content in the soil					
		substances extracted during decalcification	humic acids	fulvic acids	humic acid/fulvic acid ratio	humic acids, free and linked with mobile forms of R_2O_3 *	carbon of residual due
Tundra soil	ca. 1.0	20-30	10	30	0.3	75-100	30-40
Strongly podzolic soil	2.5-3.0	10-20	12-15	25-28	0.6	75-95	30-35
Sod-podzolic soil	3.0-4.0	ca. 10	20	25	0.8	90-95	30-35
Gray forest soil	4.0-6.0	5-10	25-30	25-27	1.0	20-30	30-35
Chernozem							
deep	9.0-10.0	5-10	35	20	1.7	20-15	30-35
ordinary	7.0-8.0	2-5	40	16-20	2.0-2.5	10-15	30-35
southern and cis-Caucasian	5.5-6.0	3-5	30-35	20	1.5-1.7	—	ca. 40
Dark chestnut soil	3.0-4.0	2-5	30-35	20	1.5-1.7	10-15	30-35
Light chestnut soil	1.5-2.0	8-10	25-29	20-25	1.2-1.5	<10	30-38
Brown soil of desert steppe	1.0-1.2	3-5	15-18	20-23	0.5-0.7	ca. 10	—
Typical serozem	1.5-2.0	ca. 10	20-30	25-30	0.8-1.0	≤10	25-35
Light serozem	0.8-1.0	—	17-23	25-35	0.7	the same	25-35
Takyr soil	ca. 1.0	5-10	7-10	20-25	0.3-0.4	ca. 5	—
Krasnozern	4.0-6.0	10-20	15-20	22-28	0.6-0.8	90-100	35-38
Mountain-meadow soil	6.0-15.0	10	15-30	28-35	0.4-0.8	—	20-40
Brown mountain-forest soil	4.0-8.0	—	25-30	30-35	0.7-0.9	10-20	20-25

* This group includes humic acids which can be extracted by 0.1 N NaOH without decalcification of the soil (mobile forms of humic acids). Expressed as a percentage of the total content of humic acids in the composition of the soil humus.

Forms of linkage of humus substances in different soils

Tyurin provisionally proposed the following classification of the linkages of humus substances:

1. Humus substances directly soluble in dilute alkalis (without preliminary removal of exchangeable calcium); these may be free, i.e. unsaturated with bases (they may be linked partly with mobile hydrated sesquioxides or, as in solonchets, with sodium) or they may consist of polymeric complexes of humic acids and fulvic acids.

2. Humus substances which are soluble in dilute alkalis only after the removal of exchangeable calcium from the soil; in this category are included polymeric complexes of humic acids and fulvic acids in linkage with calcium.

3. Humus substances soluble in dilute alkalis after alternate treatment of the soil with acid (5% H_2SO_4) and alkali; here are included complexes of humic and fulvic acids linked with relatively stable hydrated sesquioxides.

In addition, Tyurin isolated another fulvic-acid fraction soluble with the direct treatment of the soil with dilute mineral acids (0.1–0.5 N); this consists partly of free fulvic acids although for the most part it consists of salts and complex compounds with mobile hydrated sesquioxides, mainly with aluminium.

From data on the composition of humus of different soil groups, Tyurin showed the existence of the following well-defined regularities in the distribution of humus substances:

In soils with low humic-acid content—krasnozems and typical podzolic soils—humic acids are predominantly in the form of free polymeric complexes readily soluble by direct treatment with dilute alkali solutions; the content of humic acids linked with calcium and with stable sesquioxides is very small or almost negligible.

On the other hand, in soils with a high humic-acid content in the humus, such as chernozems and chestnut soils, humic acids are mainly linked with calcium, and free humic acids (and fulvic acids) are almost completely absent.

For acid soils not saturated with calcium (particularly in krasnozems and in humic-illuvial horizons), a fairly high content of fulvic acids soluble in dilute mineral acids is characteristic; this fraction is negligible in chernozem and other soils containing Ca (Table 56).

The scheme given by Tyurin for the forms of linkage between humus substances and the mineral constituents in different soils is, of course,

TABLE 56. APPROXIMATE DISTRIBUTION OF HUMIC ACIDS ACCORDING TO THEIR FORMS OF COMBINATION, EXPRESSED AS PERCENTAGES OF TOTAL HUMUS CONTENT IN TOP 20 cm (Tyurin, 1949)

Soil	Humic acids			Fulvic acids		
	soluble directly in NaOH	combined with Ca	combined with R_2O_3	soluble directly in acids	soluble directly in NaOH	dissolved together with humic acid*
Podzolic and sod-podzolic soils of the northern forest zone	16-5	0-6	4-10	6-4	20-10	14-23
Gray, slightly podzolized soils of the forest-steppe zone	6	12	7	3	19	18
Deep chernozems	0-2	23	13	2	14	17
Ordinary chernozems	0-2	22	10	3	9	16
Solonchetses of chestnut zone	8	10	5	6	16	16
Serozems	0	9	12	8	5	19
Krasnozems	12	1	2	14	24	4

* Linked with Ca and R_2O_3 , mainly the latter.

only approximate. The forms of the organo-mineral compounds in a soil under given conditions depend on the nature of the organic substances as well as on the mineral constituents (see Chapter 4, section "The role of organic matter in the formation of soil profiles").

Tyurin, examining the cause of the regular changes in the content and nature of the humic acids in the composition of the humus in soils, attributed them to differences in the natural conditions of soil formation. The enormous humus accumulation in deep (fertile) chernozems is associated with the decomposition of a large amount of root residues under conditions of maximum moisture in spring and a limited period of continuous saturation of the humus horizon. In these soils, the summer period of comparative dryness probably promotes the conversion of the ulmic acid formed into humic acid and the fixation of the latter as calcium humate.

On passing from chernozems towards the north—towards podzolized soils of the forest steppe and particularly towards podzolic soils of the northern forest zone—the periods of soil desiccation are shortened and

eventually disappear; under adequate moisture conditions processes involving the hydrolysis of organic substances are predominant. Therefore, as conditions become less favourable for the formation of humic acids, their amount decreases and fulvic acids become the predominant group of humus substances.

To the south and south-east of the chernozems, an increase in the relative content of humic acids might be expected because of the lower humidity of the climate. However, the marked decrease in the amount of plant residues entering the soil (due to the thin plant cover) and the predominance of oxidizing decomposition processes due to the high temperatures hinder the formation of humic acids. As a result of this, in soils of semi-deserts which have a low total humus content, the content of humic acids is also low. The high nitrogen content of the humus of serozems is attributed to the more active participation of bacterial plasma in humus formation in these soils. Krasnozems occupy a unique position: here, the increase in moisture is accompanied by an increase in the amount of plant residues entering the soil; this leads to the accumulation of fairly large amounts of humus substances, mainly in the form of fulvic acids combined with mobile forms of sesquioxides.

This is Tyurin's conception of the geographical regularities in humus formation. The great value of his work lies in the fact that it represents, firstly, a systematic treatment of existing data and, secondly, an attempt to explain the causes of the differences that exist in the organic matter of soils of the main soil groups of the USSR. Moreover, in this important branch of the soil-humus problem, this work, like any great work surveying a particular stage of an investigation, gives an indication of the course of future study.

It is necessary to carry out a study of the nature and properties of the separate groups of humus substances which in Tyurin's procedure for the analysis of humus composition are determined quantitatively.

The nature and properties of humus substances were discussed in Chapter 2. As can be seen from this material, the diversity of natural conditions during soil formation causes substantial differences in the nature of the humus substances formed, in particular in members of the humic acid groups.

Data on elementary composition (see Table 5), and from X-ray analysis and optical density determinations (see Fig. 10) indicate that the nature of humic acids becomes more complex on passing from podzolic soils to chernozems; the aromatic carbon net in humic acids is expressed more clearly, while at the same time the number of side radicals decreases.

In so far as the net of aromatic carbon constitutes a hydrophobic part of the molecule and the hydrophilic properties are determined by the atomic groups in side radicals, the ratio of aromatic to aliphatic structures in the molecule determines the hydrophilic properties of humic acid as a whole; this is shown by the swelling ability, the degree of dispersion, and also by the behaviour towards electrolytes (see Table 21). The tendency of humus substances to form intra-complex compounds (chelates) with iron, aluminium and certain other polyvalent cations, is due to the presence of hydrophilic groups in the side radicals.

In Chapter 4, data were given which showed that fulvic acids and fulvic-like humic acids (for example, humic acids from the humus-illuvial horizon of a strongly podzolic soil characterized by a high content of hydrophilic groups) have the strongest tendency to form iron-humus complexes of the chelate type. Humic acids from chernozems, which possess the most clearly expressed aromatic carbon net with the least number of side chains (see Fig. 46), do not exhibit any ability to form iron-humus complexes of the chelate type.

Humus of tundra soils

Owing to low temperatures and high moisture content of the soils, the tundra zone, which occupies the vast territory in the extreme north of the European and Asiatic parts of the USSR, is characterized by very distinctive conditions of soil formation. This is due not so much to the amount of precipitation as to the small evaporation. The excessive moisture favours reducing processes, in particular soil gleying. The permanently frozen ground or permafrost is very important in the formation of humus in tundra soils, for it influences the way that organic residues are transformed, the nature of the humus and its distribution in the profile.

The soil forming process in the tundra zone develops chiefly under a canopy of moss, lichen and brushwood, with very little or no grass vegetation. The microflora in tundra soils is poor both in numbers and in species composition, and is characterized by reduced activity; Rybalkina (1952) gives experimental data and references.

These conditions—limited additions of plant material to the soil, poor microflora, with unfavourable hydrothermal conditions for its activity—cause tundra soils to have a low humus content.

Investigations on the nature of tundra humus are not numerous, but indicate that, owing to the diversity of natural conditions in the formation of the soils, there are substantial variations both in the total humus

TABLE 57. CONTENT AND COMPOSITION OF HUMUS IN TUNDRA SOILS

Soil and locality	Depth of sampling cm	Organic C %	N %	C/N ratio	Carbon of humus fractions, as % of total soil organic C			Author
					humic acids	fulvic acids	humic acid/fulvic acid ratio	
Tundra surface — gleyey loamy soil, Vorkuta	0-8	26.7	1.05	25.4	6.5	24.2	0.27	Baranovskaya (1952a)
	10-16	2.2	0.154	14.3	8.7	27.8	0.31	
	16-27	0.8	0.049	16.3	3.1	38.8	0.08	
	27-45	0.9	0.068	13.3	3.0	31.0	0.09	
Gleyey-podzolic tundra soil, Salekhard	0-5	0.95	0.08	11.9	14.2	25.2	0.58	Kosheleva and Tolstukhina (1957)
	10-15	0.76	—	—	5.9	21.7	0.27	
Tundra soil, Northern Yakutiya	6-10	12.17	0.95	12.8	25	36.2	0.69	Karavaeva and Targul'yan (1960)
	35.40	4.74	0.35	13.5	25.3	23.7	1.07	

content and in its composition. Data characterizing the humus of virgin tundra soils is given in Table 57.

The tundras of Vorkuta and Salekhard are distinguished by their low humus content, and low humic acid content of the humus. In the tundra of Northern Yakutiya, even at a depth of 35–40 cm, an organic carbon content as high as 4.74 per cent has been recorded. A fairly high percentage of humic acids in the humus of this soil is noteworthy; in addition at the depth of 35–40 cm, the humic acid carbon/fulvic acid carbon ratio is higher than the ratio for the 6–10 cm horizon, exceeding unity. The authors (Karavaeva and Targul'yan, 1960) explain this by proposing that humus substances migrate from the horizons in which they are formed towards the cold front of the permafrost where they are stabilized by anaerobic conditions, low temperature and the heavy mechanical composition of the layer overlying the frost.

Humus of strongly podzolic soils

Podzolic soils, which occur in a zone situated to the south of the tundra zone, occupy a large area both in the European and in the Asiatic parts of the USSR. The zone is characterized by a great diversity of climatic conditions, vegetation and parent material. This is reflected in the soil cover, which is represented mainly by soils of the podzolic or sod-podzolic type developing during the simultaneous action of two processes—podzolic-forming and sod-forming processes. The relationship between these two processes very clearly affects the nature of the humus.

A number of investigations have been devoted to the study of the laws governing humus formation during the various manifestations of the podzol-forming and sod-forming processes. Results from these investigations are given in Tables 54, 55 and 56, Fig. 57, and also in the review articles by Tyurin (1949, 1951) and Kononova (1963).

Here we shall limit discussion to data from only a few soil profiles.

The humus of a strongly podzolic soil with signs of surface gleying, overlying very fine clay loam (Komi ASSR), was investigated. The soil occurred under spruce forest; among the underwood were spruce, birch, cedar and *Abies*. The shrub layer consisted of bilberry; the moss cover consisted of *Hypnum* and occasionally *Sphagnum*. A_0 horizon—moss litter, 0–8 cm; A_2 —podzolic horizon, 8–12 cm; B_1 —illuvial horizon, 12–32 cm; the latter shows clear evidence of humus infiltration at the surface (Table 58). The B_2 horizon, 32–60 cm—very fine sandy loam of nut-like structure with silica admixture. The soils were acid; the A_0 , B_1 and B_2

TABLE 58. THE CONTENT AND COMPOSITION OF HUMUS OF STRONGLY PODZOLIC SOIL

Horizon and depth (cm)	Humus (%)	C of humus fractions expressed as % of the total organic C					Humic acid/fulvic acid ratio	Mobile forms of humic acids		
		extracted with ethanol-benzene	extracted during decalcification	humic acids*	fulvic acids	residue		total	% of total amount of humus	% of total amount of humic acid
<i>A</i> ₂ 8-12	2.31	17.9	11.2	13.5	23.9	31.3	97.8	0.56	12.7	94.4
<i>B</i> ₁ 15-20	3.49	9.9	20.8	16.8	33.2	18.3	99.0	0.51	15.3	91.9
<i>B</i> ₂ 25-30	1.07	17.7	16.2	14.5	21.0	25.8	95.2	0.69	—	—

* In this soil and in the following soils the sum of the content of humic and fulvic acids is given (extracted with 0.1 N NaOH after decalcification of the soil followed by alternate treatment of the soil with 0.1 N H₂SO₄ and 0.1 N NaOH).

horizons are of pH 5.2 and the podzolic horizon was of pH 4.3. The exchange capacity of the litter was 46.9 m eq per 100 g soil; in the mineral horizons the sum of bases (Ca + Mg) was negligible, amounting to only 1.2–2.5 m eq.

Northern podzolic soils are characterized by low microbiological activity; this can be attributed, on the one hand, to the low number of micro-organisms in them (see data of Table 47 and Fig. 52) and, on the other hand, to the unfavourable hydrothermal conditions (insufficient heat and excessive moisture).

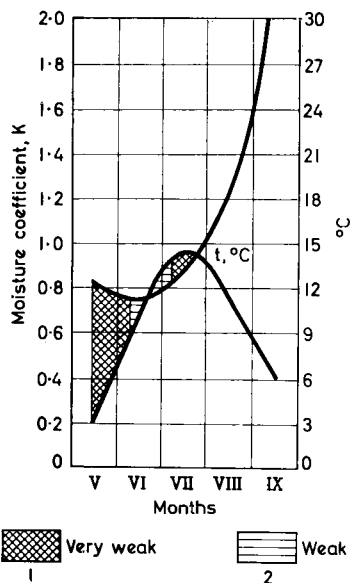


FIG. 58. Scheme of the possible intensity of biological activity in a northern podzol.

From data given in Chapter 5 on the dependence of microbial activity on the hydrothermal conditions, we have compiled schemes for the possible intensity of biological activity in the major soil-climatic zones of the USSR.

In Fig. 58 such a scheme for a northern podzolic soil is given; from this scheme it can be seen that, here, the activity of micro-organisms is limited to the short summer period and, in general, may be classed as weak.

The processes of humus formation in these soils proceed slowly with the formation of intermediate products of decomposition. The acid reaction of the soil medium promotes the formation of humus substances of the fulvic-acid type. Humic acids resemble the latter; this can be seen from

data on the elementary composition (see Table 20), from X-ray analysis (Kononova, 1956), from optical density data (Fig. 10, Table 59) and from the behaviour towards electrolytes (see the data given and also Table 21).

TABLE 59A. OPTICAL DENSITY (D) OF HUMATES AND FULVIC ACIDS FROM STRONGLY PODZOLIC SOILS

Investigated materials	Values of optical density (D) at wave-length $m\mu$						
	726	665	619	574	533	496	465
Na humate from strongly podzolic soil:							
horizon 8–12 cm	0.10	0.16	0.26	0.37	0.55	0.71	0.88
horizon 15–20 cm	0.08	0.12	0.19	0.30	0.44	0.61	0.76
horizon 25–30 cm	0.08	0.14	0.21	0.31	0.43	0.57	0.72
Fulvic acids (preparation by Ponomareva):							
No. 1	0.03	0.06	0.11	0.17	0.25	0.39	0.53
No. 2	0.13	0.17	0.20	0.30	0.42	0.60	0.77

TABLE 59B. COAGULATION (PRECIPITATION) VALUES OF HUMATES AND FULVIC ACIDS FROM STRONGLY PODZOLIC SOILS

Investigated materials	Beginning of coagulation (CaCl ₂ in m eq per 1 of solution)	Complete coagulation	
		time (hrs)	CaCl ₂ (m eq per 1 of solution)
Na humate from strongly podzolic soil. Forest horizon 8–12 cm	20	3	38
Fulvic acids (Ponomareva)	25	6	40

Accordingly, it can be assumed that in their functions the humic acids from strongly podzolic soils have features in common with fulvic acids. Here, apparently, both groups are mobile, capable of forming complex and intra-complex compounds soluble over a wide range of acid and alkaline pH values with non-silicate forms of iron and aluminium. These compounds are readily translocated down the soil profile in the descending water current and participate in the formation of an illuvial horizon, where, under the influence of bases, as a result of physical absorption and by the

mutual coagulation of oppositely charged colloids, the coagulation of organic and mineral colloids takes place.

Owing to the absence of exchangeable Ca^{2+} and Mg^{2+} , humus substances occur either in a free state or combined with mobile forms of sesquioxides; by treatment of the soil sample with 0.1 N NaOH without preliminary decalcification all the humic acids are separated completely (see Table 58, columns 9 and 10).

The high mobility of the organic matter of strongly podzolic soil is also evident from the large amount of substances passing into solution during treatment of the soil with dilute acid; this amounts to 11–20 per cent of the total humus content (see Table 58, column 3).

Comparing our data characterizing the nature of humic acids of strongly podzolic soil with Ponomareva's data (1940), also for strongly podzolic soil, a close similarity can be seen between them. Thus, Ponomareva shows that during precipitation of humic acids from alkali extract, it is difficult to separate them from other organic substances (fulvic acids) remaining in the acid solution. Both groups are as if linked by a chain of gradual transitions so that no distinct boundary exists between them. According to Ponomareva the formation of humic acids of this type is promoted under natural conditions of slow decomposition of organic substances; because of this, the process is checked at earlier stages of condensation and self-condensation.

From the data given, it can be seen that the course of humus formation, the amount and composition of the humus and also the nature of the humic acids in strongly podzolic soil are determined by the following factors:

1. The special nature of the sources of humus substances, which in these soils are predominantly leaf-fall, mainly of coniferous species, and the moss cover; the acid reaction of this soil favours the decomposition of residues by fungi.
2. The small population of soil micro-organisms and their low biochemical activity.
3. The unfavourable hydrothermal conditions for microbial activity (insufficient heat, excessive moisture). These factors produce a retarded humification of the plant residues, an accumulation of intermediate decomposition products in the soil, a low humus content and the predominance of fulvic acids over humic acids in the composition of the humus.
4. The excessive soil moisture at the time of the new formation of humus substances, resulting in the appearance of humic acids with slight

aromaticity associated with a predominance of peripheral chains; they are highly dispersed and do not coagulate easily so that their value as structure-forming agents is low.

The improvement of the organic matter of strongly podzolic soil for agriculture is possible only by bringing about a fundamental change in soil formation in the direction of a development of the sod process. We come now to a consideration of the organic matter of sod-podzolic soils.

Humus of sod-podzolic soils

Sod-podzolic soils overlying heavy clay loam from the Prechisten district of Yaroslav region will serve as an example of this type of soil. Some data from Abramova's description are as follows: Profile No. 7 was situated in a mixed forest where spruce predominated and birch and aspen occurred. The ground cover consisted of barberry and various grasses; the moss cover was weakly developed. Thus, the sources of humus were not only the leaf-fall of coniferous species and the moss cover but also the leaves of deciduous trees and grass vegetation.

The second profile, No. 10, was exposed in old cultivated soil, which was manured from time to time, and periodically was under perennial grasses with clover. The effect of cultivation was clearly visible in the morphological structure of the soil (less clearly expressed A_2 horizon) and in its chemical properties (high humus content, high exchange capacity and the absence of exchangeable H^+).

The reaction of the soil under forest was acid (pH 5.07–5.4) while that of the cultivated soil was close to neutral (pH 6.0–6.3). In the soil under forest the exchange capacity in the 4–7 cm layer was 11.65 m eq per 100 g soil and in the lower layers was 6–7 m eq; of this $Ca^{2+} + Mg^{2+}$ amounted to approximately 50 per cent. In the cultivated soil, the exchange capacity was 7.66 m eq in the top layer and increased with increasing depth to 9–10 m eq; in this soil, exchangeable H^+ was entirely absent from the profile. From the profile descriptions and from the results of chemical analyses it follows that, at the present day, these soils have reached the sod stage of soil formation; the preceding podzolic stage is indicated in the forest soil by a well-developed A_2 horizon.

It can be assumed from the data of microbiological investigations, that the number of micro-organisms and their biochemical activity are greater in sod-podzolic soils than in strongly podzolic soils, the hydrothermal conditions being much more favourable for microbial activity in the former. An approximate scheme of the intensity of biological activity is given

in Fig. 59, which shows that in these soils activity can be quite intensive over a fairly long period.

On the whole, the change in the conditions of humus formation in sod-podzolic soil compared with those in strongly sod-podzolic soil results in a considerable accumulation of humus in the 4–7 cm horizon.

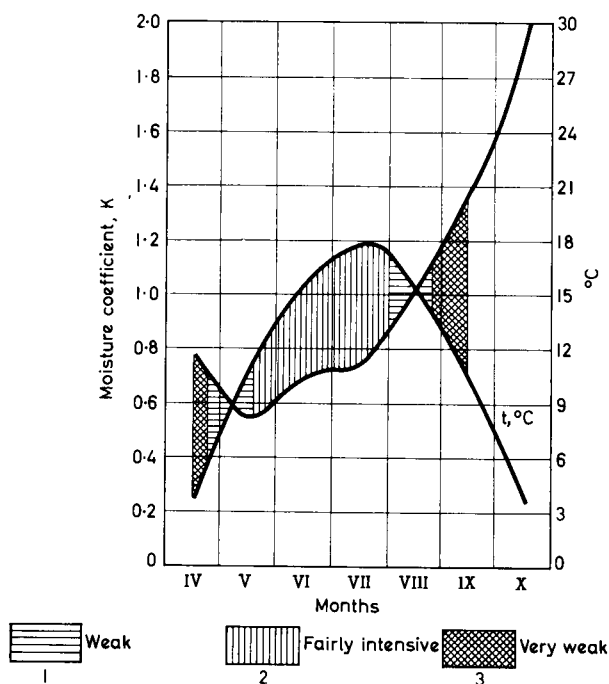


FIG. 59. Scheme of the possible intensity of biological activity in sod-podzolic soil.

The total reserve of plant residues under forest (Fig. 60) is again fairly large but here it accumulates mainly in the form of litter. Most of the roots belong to woody vegetation; these are mainly coarse and thick while the fine roots, which are most important in humus formation, amount to only 10 per cent of the total reserve of plant residues. In cultivated soil (Fig. 61), the total reserve of roots is not great but they are all fine roots and so more valuable for the formation of humus substances.

A change in the conditions of humus formation compared with the conditions in strongly podzolic soil would inevitably affect the composition of the humus: in the A_1 horizon of sod-podzolic soil, the absolute and relative contents of humic acid increase and, correspondingly, the humic acid/fulvic acid ratio increases to 0.77–0.79. In the A_2 horizon and below,

it remains at 0.5–0.58 (as in strongly podzolic soil). The humic acids are represented mainly by free forms and by forms in combination with mobile sesquioxides as they are completely extracted by a single treatment of the soil with 0.1 N NaOH (see Table 60, columns 7, 12, 13).

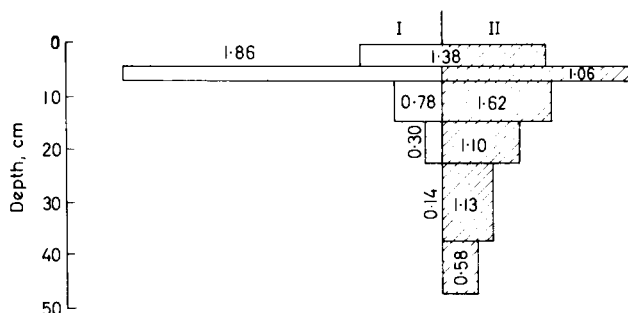


FIG. 60. Reserve of organic matter in sod-podzolic soil (Yaroslav region). Spruce forest, Profile No. 7.

I. Roots; II. Humus. Total amount of roots per sq m of the soil profile is 3.08 kg, of which fine roots amount to 0.47 kg, and litter to 1.38 kg; the total amount of humus per sq m of the profile is 5.49 kg.

The humus as a whole acquires a somewhat greater stability; the amount of organic substances extracted during decalcification decreases. The only exception is the podzolic horizon A_2 of forest soil, in which the humus

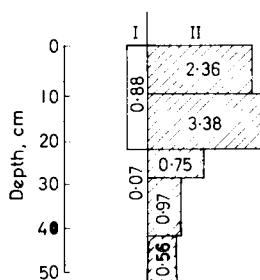


FIG. 61. Reserve of organic matter in sod-podzolic soil (Yaroslav region). Arable soil, Profile No. 10.

I. Roots; II. Humus. Total amount of roots per sq m of the soil profile is 0.95 kg, of which fine roots amount to 0.95 kg; the total amount of humus per sq m of the profile is 8.02 kg.

retains a high degree of mobility; here the amount of substances extracted during decalcification is 11.2 per cent of the total amount of humus (Table 60).

TABLE 60. PERCENTAGE CONTENT AND COMPOSITION OF HUMUS OF SOD-PODZOLIC SOILS

Soil, depth of horizon (cm)	C	N	C: N	Hu- mus	C of humus fractions expressed as % of total organic C						Humic acid/ fulvic acid ratio	Mobile forms of humic acids	
					extracted with ethanol- benzene	extracted during decalcifi- cation	humic acids	fulvic acids	residue	total		% of total amount of humus	% of total amount of humic acids
Forest; Profile No. 7:													
A_1 , 4-7	4.03	0.26	15.5	6.93	12.2	2.0	22.3	28.3	34.7	99.5	0.79	21.0	100.0
A_1, A_2 7-15	0.98	0.08	12.3	1.69	12.2	11.2	15.3	26.5	34.8	100.0	0.58	not det'd	—
A_1, A_2 15-23	0.58	0.06	9.7	1.00	17.2	1.7	13.8	24.1	41.4	98.2	0.57	15.5	100.0
A_2 27-38	0.30	0.03	10.0	0.52	23.4	3.3	13.3	26.7	33.3	100.0	0.50	not det'd	—
Arable; Profile No. 10:													
A_1 0-10	1.16	0.14	8.3	2.00	6.3	0.9	22.3	29.2	38.8	97.5	0.77	20.0	89.5
10-23	1.21	0.13	9.3	2.08	12.0	4.9	16.9	28.9	37.2	99.9	0.58	16.9	100.0
A_1, A_2 23-29	0.52	—	—	0.89	14.5	6.7	15.4	28.8	34.6	100.0	0.54	not det'd	—

Important changes occur also in the nature of the humic acids; this can be seen from the optical density *D* of the humate solutions, which is considerably higher than that for humic acids from strongly podzolic soil (Table 61A).

This may be explained by the greater degree of condensation of the aromatic rings in them. Correspondingly, the number of peripheral chains and, simultaneously, the hydrophilic nature and the degree of dispersion decrease. Therefore, compared with the humic acids of strongly podzolic soil, those of sod-podzolic soils are less resistant towards electrolytes (see Table 61B and also Table 21).

TABLE 61A. OPTICAL DENSITY (*D*) OF SOLUTIONS OF HUMATES FROM SOD-PODZOLIC SOILS

Soil, depth of horizon (cm)	Values of <i>D</i> at wave-length $m\mu$						
	726	665	619	574	533	496	465
Forest; Profile No. 7:							
<i>A</i> ₁ , 4-7	0.22	0.34	0.50	0.72	0.98	1.29	1.58
<i>A</i> ₁ , <i>A</i> ₂ , 7-15	0.25	0.39	0.57	0.81	1.06	1.40	1.75
15-23	0.31	0.49	0.67	1.00	1.23	1.62	1.93
Arable; Profile No. 10:							
<i>A</i> ₁ , 0-10	0.16	0.28	0.39	0.57	0.75	1.00	1.21
<i>A</i> ₁ , 10-23	0.16	0.26	0.38	0.55	0.75	1.00	1.21
<i>A</i> ₁ , <i>A</i> ₂ , 23-29	0.17	0.27	0.41	0.59	0.84	1.09	1.33

TABLE 61B. COAGULATION (PRECIPITATION) VALUES OF HUMATES FROM SOD-PODZOLIC SOIL

Materials investigated	Beginning of coagulation (m eq CaCl ₂ per 1 of solution)	Complete coagulation	
		time (hrs)	m eq CaCl ₂ per 1 of solution
Na-humates from forest soil:			
from 4-7 cm layer	12	2	20
from 7-15 cm layer	9	2	14

The decrease in the degree of dispersion of humic acids of sod-podzolic soil, compared with that of humic acids of strongly podzolic soil, leads to

TABLE 62. CONTENT AND COMPOSITION OF HUMUS IN MOUNTAIN-TAIGA FERRUGINOUS SOILS OF THE CHITINSK REGION
(Data of Pankova, 1961, and Wilk, 1962)

Soil, land use, No. of profile	Hori- zon	Depth of sampling (cm)	Organic C %	N %	C/N ratio	C of humus fractions, as % of total soil organic C			
						humic acids	fulvic acids	humic acid/ fulvic acid ratio	mobile forms of humic acids*
Mountain-taiga ferruginous soil under forest, profile 97	A ₁	2-5	2.97	0.13	22.7	14.5	28.3	0.51	100.0
	B	10-20	1.38	0.08	17.3	10.9	18.1	0.60	100.0
	B ₂	35-45	0.63	0.04	15.8	7.9	22.2	0.36	100.0
The same soil, profile 7	A ₁	1-7	5.79	0.20	28.9	12.4	15.6	0.79	100.0
	B	7-17	1.25	0.05	25.0	6.4	36.0	0.18	100.0
	B ₂	25-35	0.64	0.03	21.3	none	59.4	—	100.0

* % of total amount of humic acids.

their greater accumulation in the soil and also to their more active participation in structure formation. It might be expected that cultivation would intensify the development of the sod process on arable soil compared with that on forest soil. However, the methods we used did not reveal any essential differences between these soils. This means that the methods of cultivation used here were not particularly effective in intensifying the natural course of the sod process to any great extent. Evidently, for its acceleration, more active interference by man is required: liming, the introduction of perennial grasses, the application of organic and mineral fertilizers.

The data of Bel'chikova characterizing the humus of podzolic soils agree with results from other investigations of soils from the European parts of the USSR, and also from Siberia and the Far East (Ponomareva and Myasnikova, 1954; Baranovskaya, 1952; Korotkov, 1957; Pankova, 1958; Makeev, 1959; Martynov, 1961; and others).

The humus of mountain-taiga ferruginized soils, fairly common in Siberia, is very unusual. Data on the composition of the humus in these soils are given in Table 62. It can be seen that the soils, although having a fairly high carbon content, are very poor in nitrogen and this is shown by the wide C:N ratio in the mineral horizons. Fulvic acids predominate in the composition of the humus, humic acids being represented by the fraction extractable from the non-decalcified soil by a single treatment with 0.1 N NaOH.

The optical density of humic acids from these soils proves to be very low, the values obtained being similar to those for a strongly podzolic soil under forest in northern taiga sub-zone (see Table 59A). In addition, humic acids of the mountain-taiga ferruginized soils are highly dispersed; even the addition of large amounts of CaCl_2 to the Na humates does not cause a precipitate (gel) to form.

Iron complexes of the chelate type are present in mountain-taiga soils, and this may be because fulvic acids and fulvic acid-like humic acids, which have a tendency to form these complexes, predominate in the humus composition. Titova (1962), who showed this, treated the soil with 0.1 N NaF and fractionated the extract by electrophoresis. After only one treatment of the soil, the carbon of the iron-humus complexes extracted amounted to about 20 per cent of the total carbon content of the soil.

Humus of gray forest soils

Gray forest soils, occurring in the European and Asiatic parts of the USSR in conditions of moderate moisture under deciduous species, are differentiated from sod-podzolic soils by a deeper humus horizon and by the absence of an unbroken podzolic horizon.

Initial material for the formation of humus substances in these soils comes both from leaf fall and grassy vegetation. The sod process develops with different intensity in the various groups of gray forest soils and this is reflected in the character of the humus formation process. The greatest development of the sod process corresponds with the formation of dark-gray forest soils.

We come now to the results of investigations on the organic matter of dark-gray forest soil of the Shipov forest situated in the southern part of the zone of gray forest soils (Buturlin district of Voronezh region).

Profile No. 47 was situated in an area with a tree canopy of oak, maple and spindle trees. The grass cover was very sparse (mixed grasses). The litter was fairly deep (2–3 cm) consisting mainly of foliage at various stages of humification; without doubt the litter takes an active part in humus formation. According to Stepanov (1932), who studied the soils of Shipov forest, the litter has a slightly acid reaction (pH 6.43) and the soil of the A_1 and A_2 horizons is neutral (pH 6.79). The base-exchange capacity of the mineral horizons is fairly high — about 50–57 m eq, of which 85–90 per cent is due to Ca^{2+} and the remainder to Mg^{2+} . The boundary of effervescence occurs at a depth of 123 cm.

According to data from the literature (see Table 47), gray forest soils are fairly rich in micro-organisms; their activity is promoted by the temperature and moisture conditions. The moisture deficit characteristic of the zone of inadequate moisture (see data on the Kamennaya steppe) is somewhat reduced here by the influence of the forest.

Generally speaking, the conditions in gray forest soil are quite favourable for the new formation and fixation of humus substances.

The humus of dark-gray forest soil is characterized by: (1) a fairly high humus content of the upper layer (3–10 cm); (2) absolute and relative predominance of humic acids over fulvic acids, the humic acid/fulvic acid ratio being greater than unity in the upper horizons and greater, even, than 2 in the lower horizons.

The stability of the humus was especially noticeable; the amount of organic substances extracted during decalcification is relatively high only in the upper layer (3–10 cm), where they probably originate from the litter.

TABLE 63. PERCENTAGE CONTENT AND COMPOSITION OF HUMUS OF GRAY FOREST SOILS

Soil, depth of horizon (cm)	Hu- mus	C of humus fractions expressed as % of the total organic C.					Humic acid/ fulvic acid ratio	Mobile forms of humic acid	
		extracted with ethanol-benzene	extracted during decalcification	humic acids	ful- vic acids	resi- due		% of total amount of humus	% of total amount of humic acids
Dark-gray soil, Shipov Forest									
	10-55	3.6	10.5	28.2	25.4	32.0	1.11	9.3	33.1
	A ₀ 3-10								
	A ₁ 12-19	4.0	6.2	36.6	23.2	29.4	1.57	6.5	17.8
	A ₂ 23-30	5.2	2.2	47.1	19.7	24.0	2.40	3.1	6.5
	B ₁ 34-42	6.2	4.2	44.7	18.1	24.5	2.47	2.1	4.8
Gray-podzolic soil, Tula region									
	4.95	—	—	27.5	29.6	—	0.93	—	—
	A ₀ 0-10								
	A ₁ 14-24	—	—	39.6	29.5	—	1.34	—	—
	A ₂ 26-32	—	—	33.8	32.3	—	1.05	—	—

A large proportion of the humic acids is in combination with Ca^{2+} and Mg^{2+} , as they are extracted from the soil by alkali only after decalcification. Only in the 3–10 cm and 12–19 cm horizons is the amount of mobile forms of humic acid as much as 33.1 and 17.8 per cent respectively of their total amount; apparently these are free humic acids leached out of the litter. It will be remembered that in strongly podzolic soils and sod-podzolic soils, humic acids are extracted completely by a single treatment of the soil with 0.1 N NaOH.

The nature of the humic acids also changes considerably: solutions of humates from dark-gray forest soil have a higher extinction coefficient than those from sod-podzolic soils. Moreover, the optical density of humic acids from the lower horizons is higher than that of humic acids from the upper horizons (Table 64A).

TABLE 64A. OPTICAL DENSITY (D) OF HUMATES FROM DARK-GRAY FOREST SOIL

Depth of layer (cm)	Values of D at wave-length $m\mu$						
	726	665	619	574	533	496	465
3–10	0.24	0.41	0.59	0.89	1.25	1.63	2.01
12–19	0.32	0.55	0.78	1.14	1.51	2.00	2.45
23–30	0.39	0.62	0.89	1.29	1.72	2.30	2.70
34–42	0.43	0.71	1.01	1.39	1.84	2.40	2.85

TABLE 64B. COAGULATION (PRECIPITATION) VALUES OF SOLUTIONS OF HUMATES FROM DARK-GRAY FOREST SOIL

Depth of horizon (cm)	Beginning of coagulation (m eq CaCl_2 per 1 of solution)	Complete coagulation	
		time (hrs)	CaCl_2 (m eq per 1 of solution)
3–10	7	2	16
23–30	4	2	6

These data together with data on the elementary composition (see Table 20) and on X-ray analysis (Kononova, 1956) indicate that humic acids of dark-gray forest soil possess a fairly well-expressed aromatic ring

due evidently to the moisture regime and the neutral reaction. Consequently, the humic acids of dark-gray forest soil are even more sensitive to electrolytes than those of sod-podzolic soils (see data given and also Table 21).

It can be seen from the data given that humic acids of the upper horizons are distinguished from those of the lower horizons by their higher degree of dispersion; in accordance with this their threshold of coagulation is higher than that of the lower horizons (Table 64B).

The observed differences in the composition of the humus and in the nature of the humic acids between the upper and lower parts of the forest-soil profile are, in our opinion, explicable by the history of the Shipov forest. Probably, in the past, there were periods of forest clearance and colonization of the area by meadow-steppe vegetation. At a later period — during the re-establishment of forest — the latter exerted an influence on the upper soil layers by inducing soil degradation through the action of organic substances of the litter leached into the soil by descending water currents; the humus of the lower parts of the profile retained features characteristic of chernozem soils.

From the data in Table 63, it follows that the humus and nitrogen contents of the gray forest soil (Tula region) are lower than those of the dark gray forest soil (Shipov region). Evidence of the podzol-forming process is provided by the lower content of humic acids and the higher content of fulvic acids in the humus composition, as a result of which, the humic acid/fulvic acid ratio is considerably lower in gray forest podzolized soils than in dark gray forest soils.

The laws governing humus formation in gray forest soils which we have noted remain in general valid for other examples of the same type of soil, both in the European part of the USSR and also in Siberia and in the Far East (Sokolov and Sudnitsyna, 1961; Makeev, 1959; Naumov, 1960; Budina, 1961; Semina, 1961).

Humus of chernozems

Chernozem soils occupy a large area in the USSR, extending in a continuous belt through the whole European part from the western frontiers to the east. A considerable area in the Asiatic part of the USSR is also occupied by chernozem soils, particularly in the southern part of the Western Siberian lowland and in the northern part of Kazakhstan.

The diversity of natural conditions influences the formation of chernozems, and, in particular, the nature of their humus.

The formation of chernozems is associated with the development of mixed herbaceous steppe vegetation, which has a vigorous root mass penetrating into deep horizons. The root mass is humified under climatic conditions in which the ratio of atmospheric precipitation entering the soil to moisture evaporating from the surface approaches unity.

To give an example of the state of the organic matter in ordinary chernozems, we shall examine data for the Kamennaya steppe (Voronezh region). The objects of the investigation were a natural steppe reserve (fallow since 1885), cultivated soils and soil under a forest plantation. All the soils were situated on land belonging to the Dokuchaev Institute of Agriculture.

Profile No. 45 was on uncut meadow-chernozem steppe under grass vegetation in which *Calamagrostis*, *Bromus* and *Stipa* species were dominant. On the surface there was a considerable quantity of grass litter amounting to 0.5 kg of air-dry matter per sq m. The upper soil layer was densely interwoven with fine grass rootlets.

Profile No. 75 was on soil cultivated for a long period and situated between forest belts. The soil was ordinary chernozem which, at the time of profile establishment, was planted with winter wheat undersown with lucerne and *Agropyron cristatum*.

Profile No. 77 was on ordinary chernozem under a 50-year-old forest belt; the width of the belt was 106.5 m. Oaks and maples were dominant in the area and the grass cover was sparse. The litter, which had a depth of 3 cm, consisted of woody litter, mainly of leaves in various stages of humification.

The investigated soils were heavy loams overlying yellow-brown loamy deposits. The soils were neutral within a pH range of 7.2–6.8. A characteristic of the soils was the high exchange capacity of 56–58 m eq, 56 m eq being due to Ca^{2+} and 2 m eq to Mg^{2+} .

The effect on this soil of the forest belts was reflected in some of the morphological features such as the boundary of effervescence, which is somewhat lower here due to the increased soil moisture (Baiko and Gorbunenko, 1949).

The chernozems of the Kamennaya steppe are without doubt biologically active (see Table 47).

In Fig. 62, an approximate scheme is given of the possible intensity of biological activity for Kamennaya steppe conditions. The seasonal variations in moisture produce a characteristic rhythmical pattern of biological activity, an increase in the activity of micro-organisms (at moistening) alternating with a depression (at drying). As already mentioned, these conditions bring about the formation of humus substances and prevent them

from being drawn into new biological cycles. The high exchange capacity of ordinary chernozems also favours the preservation of humus substances in the form of organo-mineral compounds. The conditions of soil forma-

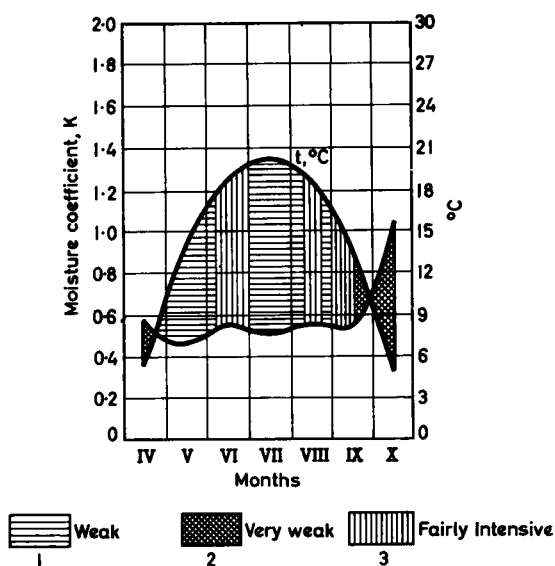


FIG. 62. Scheme of the possible intensity of biological activity in ordinary chernozem

TABLE 65. PERCENTAGE HUMUS CONTENT OF ORDINARY CHERNOZEM OF THE KAMENNAYA STEPPE UNDER DIFFERENT MANAGEMENT

Hori- zons	Steppe (uncut)	Steppe (cut)	Forest belt	Winter cereal undersown with grasses
A_0	12.64	12.97	11.32	8.26
A_1	8.88	9.89	9.96	8.26
A_2	7.43	7.40	7.6	6.07
B_1	7.07	4.88	5.92	4.58
B_2	3.37	3.33	3.17	3.47
B_3	1.27	1.27	1.81	2.25

tion of the Kamennaya steppe eventually lead to the accumulation of a considerable amount of humus (Table 65).

The percentage of humus in soils varies to some extent with the type of land utilization; in the upper horizons under uncut fallow and under

the forest belt, the humus content, because of the concentration of plant residues, is greater than in cultivated soil.

The higher percentage of humus in soils under forest plantations was demonstrated by several investigators (Usov, 1938; Tumin, 1930; Baiko and Gorbulenko, 1949; Glotova, 1950, 1952; Zonn and Sokolov, 1960). However, when the humus reserve is calculated in weight per unit area the variations in humus content under different types of land management are evened out (because of the large volume weight of cultivated soils compared with that of virgin soil and forest soil).

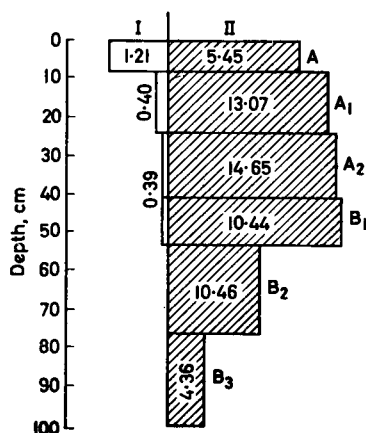


FIG. 63. The reserve of organic matter in ordinary chernozem of the Kamennay steppe. Uncut old fallow. Profile No. 45.

I. Roots; II. Humus. Total amount of roots per sq m of the soil profile—2 kg; total amount of humus per sq m in the 0–100 cm layer—58.43 kg; in the A_0 , A_1 , A_2 horizons—33.17 kg; in the 0–25 cm layer—19.38 kg.

The distribution of humus and root residues in the individual layers is shown in Figs. 63, 64 and 65.

Chernozems with a high humus content have a characteristic humus distribution; large reserves accumulate throughout the profile down to a depth of 1 m. The humus reserve in the arable soil differs only slightly from that of the virgin steppe probably due to the high level of soil improvement brought about at the Institute of Agriculture.

The composition of humus of ordinary chernozem (Table 66) is characterized by a high absolute and relative content of humic acids compared with that of fulvic acids; the humic acid/fulvic acid ratio varies from 1.5 to 2.0 or even higher.

We were unable to find any essential differences in the ratio between the main groups of humus substances under different soil utilization, hence we shall only consider data of the investigated objects—uncut steppe and cultivated soil.

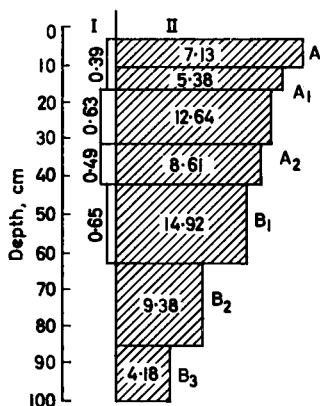


FIG. 64. The reserve of organic matter in ordinary chernozem of the Kamennaya steppe. Forest belt. Profile No. 77.

I. Roots; II. Humus. Total amount of roots per sq m of the soil profile—2.16 kg; total amount of humus per sq m in the 0–100 cm layer—62.69 kg; in the A_0 , A_1 , A_2 horizons—33.76 kg; in the 0–25 cm layer—20.09 kg.

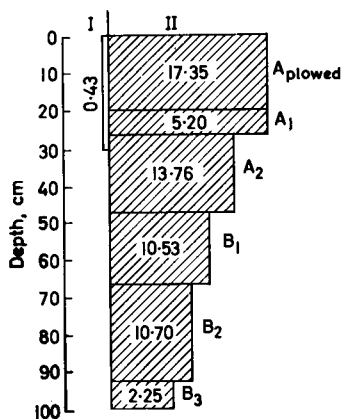


FIG. 65. The reserve of organic matter in ordinary chernozem of the Kamennaya steppe. Winter cereal undersown with grasses. Profile No. 75.

I. Roots; II. Humus. Total amount of roots per sq m of the soil profile—0.43 kg; total amount of humus per sq m in the 0–100 cm layer—59.79 kg; in the A_0 , A_1 , A_2 horizons—36.31 kg; in the 0–25 cm layer—21.68 kg.

TABLE 66. PERCENTAGE COMPOSITION OF HUMUS OF ORDINARY CHERNOZEM OF THE KAMMENNAYA STEPPE UNDER DIFFERENT MANAGEMENT

Soil utilization; depth of horizon (cm)	C	N	C:N	C of humus fractions expressed as % of the total organic C						
				extracted with ethanol-benzene	extracted during decalcification	humic acids	fulvic acids	residue	total	humic acid/fulvic acid ratio
Uncut steppe; Profile No. 45:										
A ₀ 0-7	7.35	0.54	13.6	3.7	4.1	36.3	22.4	31.2	97.7	1.61
A ₁ 10-20	5.16	0.44	11.7	4.1	2.2	38.8	22.5	31.2	98.8	1.73
A ₂ 25-30	4.32	0.36	12.0	4.2	1.2	43.5	20.4	30.0	99.3	2.13
Cultivated soil: Profile No. 75:										
A ₁ 0-20	4.79	0.37	12.9	4.0	2.2	40.5	19.6	33.5	99.8	2.07
A ₃ { 20-25	4.82	0.44	11.0	4.0	1.5	42.7	20.1	30.9	99.2	2.12
30-35	3.57	0.35	10.5	5.3	1.1	37.3	18.5	36.1	98.3	2.00

There is no doubt that the humus of ordinary chernozem is stable; this can be concluded from the small amount of organic substances extracted during decalcification.

Only a small fraction of the humic acids of chernozem is extracted by a single treatment with 0.1 N NaOH; this consist of newly formed humic acids and humic acids combined with non-silicate forms of R₂O₃ (Table

TABLE 67. AMOUNT OF HUMIC ACIDS PASSING INTO SOLUTION AT A SINGLE TREATMENT OF THE SOIL WITH 0.1 N NaOH WITHOUT DECALCIFICATION

	Uncut steppe		Cultivated soil			Forest belt		
	(cm)							
	0-7	10-20	0-20	20-25	30-35	3-8	10-16	32-37
% of total humus	9.5	5.0	1.7	2.7	0.6	9.0	14.1	5.7
% of total amount of humic acids	25.9	12.9	4.1	5.8	1.5	23.0	27.9	10.7

67). For the most part, the humic acids in these soils are combined with calcium in the form of complex compounds which are decomposed by treatment of the soil with dilute solutions of mineral acids.

The conditions of soil formation in chernozems (in particular, the limited moisture regime and neutral soil reaction) promote the formation of humic acids with a clearly expressed (compared with other soils) aromatic ring. This can be seen from X-ray analysis (Kononova, 1956), from the elementary composition (see Table 20) and from the optical density (D) (Fig. 10 and Table 68). Correspondingly, the number of peripheral chains decreases and, therefore, the hydrophilic nature is less marked; humic acids are only slightly dispersed and coagulate even with small amounts of electrolyte (see the data and also Table 21).

TABLE 68. OPTICAL DENSITY (D) OF HUMATES FROM ORDINARY CHERNOZEM

Soil utilization; depth of horizon (cm)	Values of D at wave-length $m\mu$						
	726	665	619	574	533	496	465
Uncut steppe; Profile No. 45:							
0-7	0.40	0.61	0.83	1.11	1.43	1.80	2.20
10-20	0.53	0.79	1.04	1.42	1.85	2.35	2.66
Forest belt; Profile No. 77:							
3-8	0.46	0.68	0.90	1.22	1.61	2.03	2.44
10-16	0.45	0.66	0.91	1.23	1.61	2.09	2.45
Cultivated soil; Profile No. 75:							
0-25	0.49	0.74	0.96	1.32	1.69	2.12	2.55
20-25	0.45	0.69	0.92	1.26	1.67	2.15	2.53

The complex nature of the humic acids, the presence of a large number of mineral colloids, the high exchange capacity and the predominance of exchangeable bases (amounting to 55-60 m eq per 100 g soil) in the absorption complex are all factors which favour the fixation of humus in chernozem soils, giving it the appearance of inertness, and determine its slight participation in weathering processes and its accumulation in the zone of humifying organic residues. The ease with which humic acid is coagulated by calcium in the form of "flocs" favours the formation of aggregates of granular structure which are of high agronomic value.

In differently utilized soils, some variation in the state of the humus is observed. Thus, in soil utilized under crops for a long period (Kamennaya steppe), there was, compared with meadow-chernozem soil under fallow,

a redistribution of humus in the profile and a smaller content of free (newly formed) humic acids. However, in spite of this, no essential difference in the reserves or in the composition of the humus were observed between these two differently utilized soils.

The somewhat higher coagulation-threshold values of humates from the upper horizon (0-7 cm) of steppe soils is explained by the fact that here there is an intensive new formation of humic acids. Because they are newly formed, these acids are more highly dispersed than humic acids formed previously. In our opinion, this is also the reason for a certain increase in the degree of dispersion of humic acids in the 3-8 cm layer under the forest belt.

Soil utilization; depth of horizon (cm)	Beginning of coagu- lation	Complete coagulation	
	m eq CaCl ₂ per 1 of solution	time (hrs)	m eq CaCl ₂ per 1 of solution
Uncut steppe			
0-7	7	2	11
10-20	4	2	5.5
25-35	4	2	4.5
Cultivated soil:			
0-20	4	2	4
Forest belt:			
3-8	5	2	9
17-22	4.5	2	7
32-37	4	2	5

The humus content and composition, and the nature of the humic acids differ appreciably in the various sub-types (leached, deep and fertile, ordinary, and southern chernozems). However the main criteria that characterize the humus of the chernozem type of soil formation are retained: the very thick humus horizon, the high humus content, the prevalence of the humic acid group in the humus composition (the humic acid/fulvic acid ratio is 1.5-2.0, and sometimes higher). The humic acids are mainly complex forms linked with calcium and are preferentially extracted after treatment of the soil with mineral acid solutions (Table 69).

In recent years a number of papers have published data characterizing the nature of humus in the chernozems of Siberia, Kazakhstan and the

Tuvinskaya ASSR. Some authors note that the humus composition of these soils is generally similar to that of chernozems in the European part of the USSR. However in some soils a lower humic acid content of the humus has been recorded (Emel'yanov, 1953, 1956; Kotel'nikov, 1958; Yurlova, 1958, 1959; Bogdanov, 1961; Pankova, 1961). Such differences can apparently be explained by local characteristics of soil formation.

From an examination of data characterizing the state of the organic fraction in strongly podzolic, sod-podzolic, gray forest and chernozem soils the following regularities are found:

1. The amount of humus increases in this series of soils.
2. The humic-acid content of the humus increases.
3. The stability of humus increases.
4. The molecules of the humic acids become more complex and their degree of dispersion correspondingly decreases.

We come now to an examination of data characterizing the content and composition of humus of dry and desert steppes, selecting as examples, chestnut soil, brown desert steppe soils, takyrs and serozems.

Humus of chestnut soils and solonetses in the dry steppe zone

Chestnut soils are situated in the dry steppe zone and occur south of the chernozems; this zone extends along the northern coasts of the Black and Azov Seas, along the lower reaches of the Volga and along the Urals, crossing into Kazakhstan and Western and Eastern Siberia.

The chestnut soils are characterized by a limited amount of precipitation, sharp daily and seasonal variations in the air temperature and high evaporation coefficients. Corresponding to this, hydrothermal conditions over the course of the year are generally unfavourable for microbial activity even though the soils, according to the data of investigations, have a fairly rich microflora. This was shown for chestnut soils of the Trans-Volga region in the works of A. A. and V. A. Rikhter (1925), Zakharova (1933), Krasil'nikov, Kriss and Litvinov (1936) and Ryuger (1940); see also Table 47 and Fig. 52. Using the plate method, we detected a large number of micro-organisms in the solonets of Malouzensk Station; this confirmed the data of other investigators who had observed a rich microflora in solonets of different origin (Germanov, 1933; Genkel' and Zakharova, 1930; Kudrina, 1955; Runov and Bol'shakova, 1960; Nepomiluev and Poddubnyi, 1961).

In Fig. 66 is illustrated in approximate scheme of the possible intensity of biological activity—the latter is limited to the short spring and early

TABLE 69. CONTENT AND COMPOSITION OF HUMUS OF CHERNOZEMS IN THE EUROPEAN PART OF THE USSR

Soil, land use, locality	Depth of sampling (cm)	Organic C %	N %	C:N ratio	Carbon of humus fractions as % of total soil organic C				Author
					humic acids	fulvic acids	humic acid/fulvic acid ratio	mobile forms of humic acids*	
Deep chernozem, continuous fallow, Kursk reservation	0-20	5.25	0.44	11.9	36.9	21.3	1.73	22.2	Bel'chikova
Cis-Caucasian, carbonate chernozem, arable land, Northern Osetiya	0-10	3.20	—	—	32.5	21.3	1.52	6.9	Suslova (1957)
	40-50	1.78	—	—	32.6	20.2	1.61	7.3	
Cis-Caucasian, carbonate chernozem, arable land, Rostov region	0-20	2.82	0.27	10.5	37.6	20.6	1.82	N. D.	Rudenskaya (1959)
	55-65	1.52	0.14	10.9	36.8	20.9	1.76	N. D.	
Southern chernozem, arable land, Rostov region	0-20	3.38	0.32	10.6	39.7	16.6	2.39	N. D.	Rudenskaya (1959)
	50-70	1.88	0.18	10.4	39.1	18.2	2.14	N. D.	

* % of total amount of humic acids.

summer periods. During the rest of the summer it only proceeds at a very slow rate.

The main causes of the humus content being lower in chestnut soils than in chernozems are the less vigorous vegetative cover with its corresponding smaller addition of plant residues to the soil, and the less favourable conditions for microbiological activity.

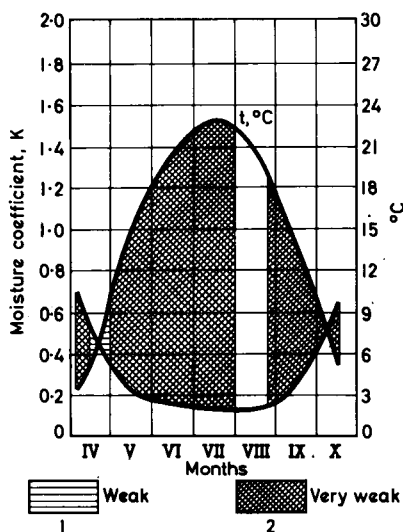


FIG. 66. Scheme of the possible intensity of biological activity in chestnut soil (Uralsk region).

Chestnut soils have a fairly high exchange capacity (30–35 m eq per 100 g soil) and the bases are predominantly calcium and magnesium. This undoubtedly promotes the humification of plant material and the fixation of humus substances in chestnut soils. In addition, the presence of exchangeable sodium brings about peptization of humus substances and their transformation into forms more available to micro-organisms and able to move in the soil profile.

From the character of their vegetative cover, their degree of humification and indications of their solonets-like properties, chestnut soils are sub-divided into dark chestnut soils, chestnut soils, and light chestnut soils. Dark chestnut soils occur in the northern part of the zone; they have formed under the *Stipa-Festuca sulcata* vegetation which is characteristic of dry steppes. The root systems penetrate to a depth of 30–40 cm and are the main source of humus; the solonets-like properties are very

TABLE 70. CONTENT AND COMPOSITION OF HUMUS IN VIRGIN CHESTNUT SOILS

Soil and locality	Depth of sampling (cm)	Organic C %	N %	C:N ratio	Carbon of humus fractions as % of total soil organic C			Author
					humic acids	fulvic acids	humic acid /fulvic acid ratio	
Dark chestnut soil, Saratov region	0-15	1.82	0.17	10.7	33.5	19.8	1.60	Kononova (1951)
	15-25	1.66	0.15	11.1	32.5	24.7	1.31	
	30-45	1.06	0.10	10.6	25.5	20.8	1.23	
Dark chestnut soil, foot-hill zone Ala-Tav	0-10	1.96	—	—	28.0	17.9	1.56	Emel'yanov (1953, 1956)
	11-20	1.15	—	—	28.3	22.3	1.27	
	30-40	0.92	—	—	26.4	23.1	1.14	
Light chestnut soil, Volgograd region	0-20	1.45	0.14	10.0	26.9	20.7	1.30	Glotova (1956)
Light chestnut soil, Karagandinsk region	0-8	1.35	—	—	18.6	13.5	1.38	Emel'yanov (1953, 1956)
	17-27	1.28	—	—	16.8	13.5	1.24	

weakly expressed. Figure 67 illustrates the reserve of humus and root mass in a dark chestnut soil.

Light chestnut soils are situated further to the south than dark chestnut soils; they are formed under *Festuca sulcata*–*Artemesia* halophytic vegetation. The solonets-like properties are more clearly expressed than in dark chestnut soils. The humus contents and compositions of dark and light chestnut soils in the European and Asiatic parts of the USSR are given in Table 70.

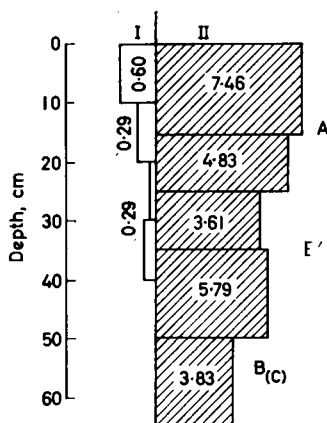


FIG. 67. The reserve of organic matter in dark chestnut soil (Ershovsk, Saratov region). I. Roots; II. Humus. Total amount of roots per sq m of the soil profile – 1.18 kg; total amount of humus per sq m of the profile – 25.32 kg.

Certain features characteristic of the humus of chernozems are retained to some extent in chestnut soils. Thus in the humus composition, the humic acid content is higher, as in chernozems, than the fulvic acid content; correspondingly the humic acid/fulvic acid ratio is larger than one. It was noted earlier that only a small fraction of the humic acids is extracted from non-decalcified chestnut soils by a single treatment with 0.1 N NaOH (see Table 32). This indicates that the humic acids form complex links with calcium (and possibly magnesium).

The elementary composition and optical density indicate that there is less condensation of the aromatic carbon net in humic acids from chestnut soils than from chernozems (Table 71, see also Table 20 and Fig. 10). It may be judged from their greater stability to the precipitating action of electrolytes that humic acids from chestnut soils contain greater numbers of side radicals with hydrophilic atomic groups.

Light chestnut soils show greater differences from chernozems in their humus composition and in the nature of their humic acids than dark

TABLE 71. OPTICAL DENSITY (D) OF HUMIC ACIDS FROM CHESTNUT AND BROWN SOILS

Soil and locality	Depth of sampling (cm)	Values for optical density wavelength m μ							Author
		726	665	619	574	533	496	465	
Chestnut soil, Valuisk Expt. Station	0-20	0.31	0.52	0.72	1.03	1.34	1.70	1.98	Bel'chikova
Light chestnut soil, Karagandinsk region	0-8	0.15	0.33	0.43	0.72	0.92	1.24	1.52	Emel'yanov (1953, 1956)
Brown desert-steppe soil, Dzhezkazgan Kazakhstan	0-10	0.15	0.33	0.49	0.70	0.92	1.19	1.40	Emel'yanov (1953, 1956)

TABLE 72. CONTENT AND COMPOSITION OF HUMUS IN VIRGIN SOLONETSES OF THE DRY STEPPE ZONE (Bel'chikova's data)

Soil and locality	Horizon	Depth of sampling (cm)	Organic C %	N %	C:N ratio	Carbon of humus fractions as % of total soil organic C		
						humic acids	fulvic acids	humic acid/fulvic acid ratio
Residual solonchak-like solonets, Saratov region	A ₁	0-12	1.23	0.12	10.3	28.3	30.1	0.94
	B ₁	12-22	1.05	0.12	8.8	26.0	25.7	1.01
	B ₂	22-32	0.84	0.08	10.5	17.9	24.9	0.72
Moderately-columnar solonets, Volgograd region Ergeni	A ₁	0-10	1.07	—	—	22.4	15.9	1.41
	B ₁	10-24	1.09	—	—	15.6	11.9	1.31
	B ₂	30-40	0.51	—	—	9.8	22.5	0.38

chestnut soils. This is partly due to the direct and indirect effect of exchangeable sodium, more of which is present in light chestnut soils than in dark chestnut soils. The effect of solonets-like properties is expressed to the greatest extent in solonetses, where the exchangeable sodium reaches 15 per cent or more of the total exchangeable bases. Another important factor in humus formation is that the vegetative cover of solonetses in the dry steppe zone (predominantly *Artemesia*, *Kochia* and *Pyrethrum*) is very sparse with deep root systems and is only a very limited source for the formation of new humus substances. On the whole, solonetses in the dry steppe zone are low in humus, and the humic acid content of the humus decreases; this can be seen from Table 72 and from comparing Table 72 with Table 70.

Analogous features inherent in the humus of chestnut soils and solonetses from the dry steppe zone of European USSR are recorded by Orlova (1959), Rudenskaya (1959) and Vishnevskaya (1959), and for the soils of Kazakhstan by Assing (1956).

Humus of brown desert-steppe soils and takyrs

The soils of the desert-steppe zone occur mainly in the territories of the central Asian republics (Uzbekskaya, Tadzhikskaya, Turkmeneskaya, and the southern part of Kazakhskaya SSR).

Because of the sparse *Artemesia*-halophytic vegetation (a limited source of humus substances) and the unfavourable hydrothermal conditions for biological activity (the average annual precipitation is 150–200 mm), the brown desert-steppe soils have a low humus content. According to Emel'yanov (1956) the reserve of roots in the profiles of brown loamy soils is about 10 tons per hectare; the reserve of humus in the one metre layer is approximately 60 tons per hectare and of nitrogen 4 tons per hectare.

Fulvic acids predominate in the humus composition of brown desert-steppe soils; the humic acid carbon/fulvic acid carbon ratio is 0.8–0.5, and in gray-brown soils decreases to 0.5–0.3 (Table 54). The optical density of humic acids from brown soils is low; typical values are of the same order as for light chestnut soils.

Takyrs are found in the south-western part of the Central Asian desert zone, which is characterized by a low precipitation (75–130 mm per annum falling mainly during the period of low temperatures from November to April). Only during a short spring period are the hydro-thermal conditions more or less favourable for the growth of higher vegetation and so for

microbial activity (Kovda, Bazilevich and Rodin, 1956). Moreover takyrs are extremely poor in micro-organisms (see Efendieva, 1956).

An important role in the formation of these peculiar soils is played by algae, which develop abundantly on the surface during the moist periods; the diversity of algal forms is shown by the work of Gollerbakh *et al.* (1956). The significance of algae in the weathering and formation of takyrs has been established by Bolyshev (1952, 1955); lichens are also important for humus formation in these soils. The organic mass is small; for the lichen-algae takyr, it is about 1 ton per hectare, only 30 per cent of which is higher vegetation (aerial parts and roots) (Ponomareva, 1956). The humus content is low, mainly because the sources of fresh organic material are very restricted and conditions are very unfavourable for humification. Ponomareva calculated that the average reserve of humus in the one metre layer is 78 tons per hectare and of nitrogen is 6.8 tons per hectare, 28 per cent being accumulated in the 0–20 cm layer.

Ponomareva considers that part of the humus in takyrs was introduced with proluvial¹ deposits. This may also explain the high nitrogen content of the humus in these soils; Ponomareva found that a fresh proluvial deposit contained about 0.4 per cent carbon and 0.088 per cent nitrogen.

The data on the humus composition of takyrs given in Table 73 show the predominance of fulvic acids, which under these conditions should probably be regarded as initial stages in the formation of humic acids. The elementary composition of humic acids from takyrs (Ponomareva, 1956) characterizes their “chemical youth”: the carbon content is only 50 per cent while the hydrogen and nitrogen contents reach 6 per cent. The C : H ratio is 8.33, i.e. lower than any other soil humic acid (see Table 20). Accordingly it may be presumed that the net of aromatic carbon is here expressed very weakly.

Humus of serozems

Serozems are situated mainly in the territories of the central Asian republics (in the Uzbekskaya, Tadzhikskaya, Turkmeneskaya and Kirgizskaya and in the southern part of Kazakhskaya SSR). A smaller area in the Kura-Araksinsk lowlands of the Caucasus is also occupied by these soils.

¹ “The term proluvial is used in USSR for dry delta sediments formed by temporarily existing rivers.” From: *A Glossary of Geographical Terms*, ed. L. D. Stamp, Longmans, 1961 (*Translators’ note*).

TABLE 73. CONTENT AND COMPOSITION OF HUMUS IN BROWN DESERT-STEPPE SOILS AND TAKYRS

Soil and locality	Depth of sampling (cm)	Organic C %	N %	C:N	Carbon of humus fractions as % of total soil organic C			Author
					humic acids	fulvic acids	humic acid/fulvic acid ratio	
Brown desert-steppe soil, Gur'evsk region	0-10	0.66	—	—	16.2	23.4	0.69	Emel'yanov (1953, 1956)
	13-23	0.46	—	—	10.3	23.1	0.45	
	23-33	0.45	—	—	15.9	24.7	0.64	
Gray-brown soil, Karakumy	0-4	0.25	0.05	5.0	20.0	40.7	0.49	Lobova (1960)
	15-20	0.20	—	—	13.4	44.2	0.30	
Gray-brown soil, Dzhungarsk Ala-Tau	0-8	0.35	—	—	14.3	35.9	0.39	Assing (1956)
	0-10	0.34	—	—	16.2	36.8	0.44	
Lichen-algae taylor, Karakumy	2-3	0.43	0.064	6.7	10.0	21.7	0.46	Ponomareva (1956)
	3-9	0.30	0.048	6.3	6.5	24.4	0.27	
	0-25	0.27	0.046	5.9	4.6	18.4	—	
Surface-solonchak-like taylor, lower reach of the Amu-Dar'	0-9	0.34	0.07	4.9	3.4	14.6	0.23	Pershina and Bykova (1959)
	22-32	0.27	0.04	6.8	7.7	16.5	0.46	

Serozems develop under conditions of fairly high temperature, the climate of the serozem zone is less continental than that of the zone where brown desert-steppe soils occur.

The special conditions of humus formation in serozem soils are determined by the intense microbiological activity. The richness of the microflora, its diversity (Kononova, 1930; Shul'gina, 1930; Korsakova, 1929; Stepa-

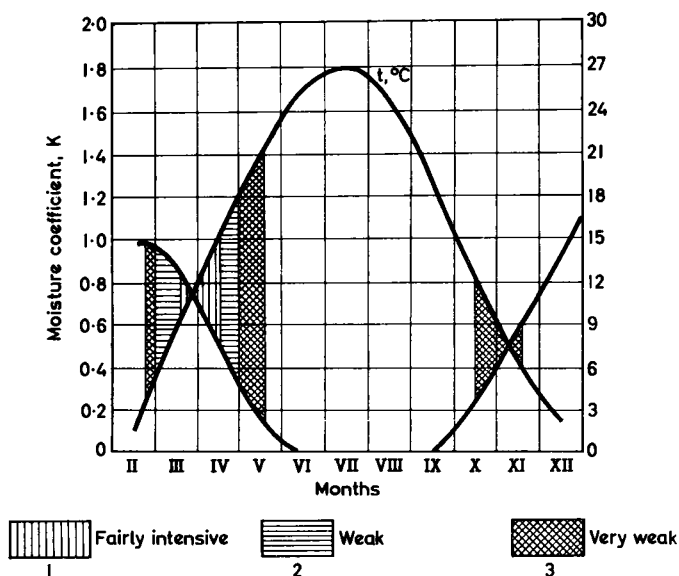


FIG. 68. Scheme of the possible intensity of biological activity in unirrigated serozem.

nova, 1928; Rokitskaya, 1927; Raznitsyna, 1947; Mishustin, 1956; Dergunov, 1959; etc.) are combined with conditions favourable for the majority of bacteria—a neutral to slightly alkaline soil reaction and a long period of seasonal high temperatures. All these conditions produce a high activity of micro-organisms provided adequate moisture is present, which is supplied in cultivated soils by irrigation.

In virgin serozems, the period of intense microbiological activity is limited to the spring. Here, however, in contrast to the soils previously examined, a short but extremely intensive flush of microbiological activity may occur during the spring period depending on the conditions of temperature and moisture (Fig. 68).

Apparently, during this short period, there occurs not only a new formation of humus substances but also their subsequent decomposition. Gel'tser (1930) found an intensive decomposition of organic substances

on unirrigated fallow during the moist spring period. In virgin serozem we are thus faced with a unique manifestation of the activity of micro-organisms—an intensive short flush during which a rapid cycle of the formation/decomposition processes of humus substances is accomplished.

The low humus content in virgin serozems is also determined by the peculiar distribution of the plant residues. According to botanists' descriptions (Korovin, Sovetkina, Kul'tiasov), the ephemeral vegetation typical of virgin serozems (perennial ephemeral species, such as *Poa bulbosa* and

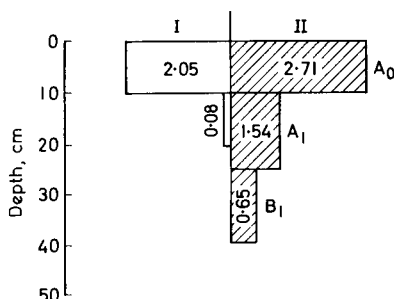


FIG. 69. The reserve of organic matter in light serozem. Virgin land of the Pakhta Aral State Farm.

I. Roots; II. Humus. Total amount of roots per sq m of the soil profile—2.13 kg; total amount of humus per sq m—4.9 kg.

Carex, and various ephemeral annuals) is very unusual in its floristic composition, in ecological adaptability and developmental rhythm; it is characterized by an overall denseness with well-developed root systems occupying the upper layer of soil which is only a few cm in thickness.

In virgin serozem, the total reserve of root residues was found to be 2.13 kg per sq m, i.e. the same as in virgin land of the Kamennaya steppe. However, in serozem, almost all of the reserve of roots is concentrated in the 0–7 cm layer; because of this they have no proper contact with the soil throughout the profile (Fig. 69).

Finally, also, the physico-chemical properties of serozems do not favour the fixation of humus, because their exchange capacity is extremely low—according to the data of Table 53, it is less than 10 m eq per 100 g soil for the mineral part of serozem.

The rapidly occurring processes of organic-matter conversion in serozems promote the formation of substances of the fulvic-acid type (see Table 74). For this reason, humic acids of serozems apparently possess a relatively weakly condensed aromatic ring with an abundance of peripheral chains. This can be concluded from the low values of the optical

TABLE 74. PERCENTAGE CONTENT AND COMPOSITION OF HUMUS OF SEROZEM SOIL

Soil and locality	Horizon (cm)	C	N	C:N	C of humus fractions as % of total organic C			
					humic acids	fulvic acids	humic acid/fulvic acid ratio	mobile forms of humic acids
Typical serozem (cotton), Ak-Kavak Exp. Sta.	0-20	0.78	0.08	9.8	20.5	23.0	0.89	5.0
Light serozem (cotton), Pakta-Aral	0-15	0.72	0.09	8.0	16.6	22.5	0.73	6.5
Serozems of the foothills and mountainous regions of Tadzhikistan (virgin):								
dark	0-20	1.48	—	—	28.8	30.0	0.95	—
ordinary	0-20	0.96	—	—	27.8	34.6	0.80	—
light	0-20	0.60	—	—	21.1	33.2	0.64	—

density (see Fig. 10) and from the high resistance towards electrolytes (Table 21).

It was shown for dark chestnut soils, brown desert-steppe soils and serozems that in the soils of dry and desert steppe there is a decrease in the amount of humus and of the humic acids in its composition. The reason for this is the change in plant cover, microbiological activity and physico-chemical properties of these soils.

Humus of krasnozems and lateritic soils

Krasnozems, which are soils of humid sub-tropical regions, occur in the USSR in Western Georgia on the Black Sea coast. The characteristic conditions for the transformation of organic matter in these soils are excessive moisture in conjunction with a long period of high temperatures (see Fig. 70). The very rich forest vegetation, which also includes evergreen species, supplies enormous amounts of plant residues in the form of leaf-fall and root masses.

Krasnozems are characterized by intensive weathering proceeding under the direct action of organic matter and under acid soil conditions. The exchange capacity of these soils is fairly high (20–30 m eq per 100 g soil); however, absorbed $H^+(Al^{3+})$ predominates.

The long duration of high temperatures, the high moisture and the abundance of plant residues suggest that, in krasnozems, conditions for

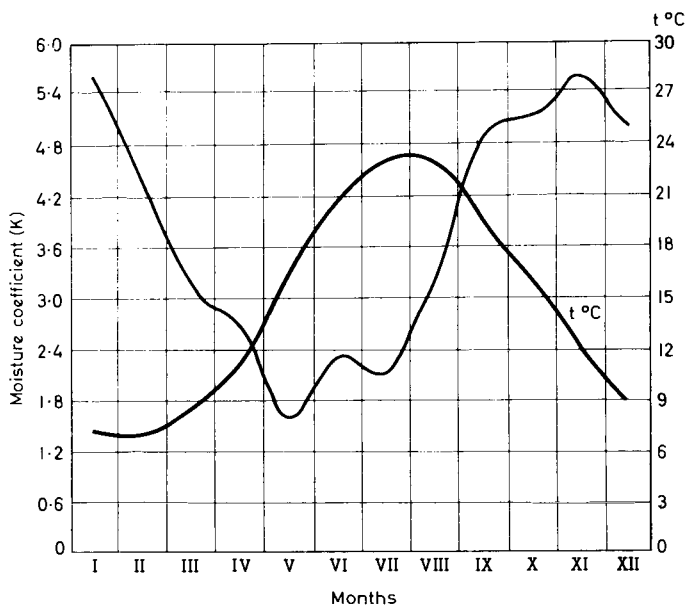


FIG. 70. Hydrothermal conditions in the humid sub-tropical zone (krasnozem zone).

intensive microbiological activity exist; accordingly, the decomposition processes of plant residues should be vigorous. Indeed, Antipov-Karataev and Prasolov (1936) consider that the high temperature and abundant precipitation in the Black Sea coastal region favour an intensive mineralization of organic residues to final products— CO_2 . This view of the intensity of organic-matter decomposition is, however, in our opinion, exaggerated. The data from microbiological investigations (Garder, 1928; Kuznetsov, 1933; Obratsova, 1936; Daraseliya, 1952) show that the number of micro-organisms in krasnozems is not so great. Microbiologists conclude unanimously that micro-organisms in krasnozems show reduced activity: Korsakova (1929), in a survey of soils of dry and moist sub-tropics, concluded that biologically the serozems of Central Asia can be regarded as active soils, and krasnozems as an example of relatively inactive soils.

The periodically excessive soil moisture, which creates anaerobic conditions, is undoubtedly a factor inhibiting the normal course of microbiological processes; it is not a coincidence, therefore, that the most active micro-organisms in krasnozems are only denitrifiers (Kuznetsov, 1933). The acid reaction of krasnozems also contributes to the weak microbiological activity.

The slow decomposition of organic matter in krasnozems can also be seen from results of our investigations: after burying clover and lucerne leaves in the soil, we found no essential changes in these residues after three weeks while in soils of the Central Belt, and particularly in irrigated serozems, legume foliage was greatly humified and digested by the soil fauna over the same period.

However, we are not in favour of extending the conclusion on the slow humification of plant residues in krasnozems to the surface leaf-fall. Direct observations on the condition of the litter under forest convince us that here the humification is very intensive; humus substances leached from the litter form the main reserve of humus in the soil.

We shall deal now with an example characterizing the state of the organic matter of krasnozem. Soil samples of krasnozems from Chakva were investigated in detail by Troitskiĭ (1949). The area of the investigation was the flat summit of a residual mountain (butte) covered by woody vegetation consisting mainly of sweet chestnut, hornbeam, beech, alder, rhododendron and lianes with a sparse ground cover (ferns and various grass species); the rich leaf-fall at the surface amounted to 1.6 kg per sq m.

The amount of roots in the soil profile (to a depth of 1 m) amounted to 10.15 kg per sq m, which is greater than the amounts of plant residues that we have found in soils of other zones. But it should be taken into account that the majority of the roots belong to woody species and that the proportion of coarse roots is one third (of the total amount); this is unfavourable for humus formation in krasnozems.

The intensive humification of the rich leaf-fall over a long period under temperature and moisture conditions favourable for microbiological activity results in the new formation of considerable amounts of humus substances which are subsequently leached out by percolating rainwater and enter the soil layers (Fig. 71).

Actually, the total amount of humus in krasnozems is fairly high: for the whole depth of the soil profile it amounts to 30 kg per sq m; this value is comparable with that of the humus reserve of dark chestnut soil, but with regard to the composition of the humus these soils differ markedly. The special conditions of humus formation in krasnozems—the formation

of humus substances in the litter, the excessive moisture and the acid reaction—give the humus features of similarity with the humus of podzolic soils (see Table 75).

In the composition of humus of krasnozems there are much lower amounts of humic acid than of fulvic acid; the humic acid/fulvic acid ratio is always less than unity.

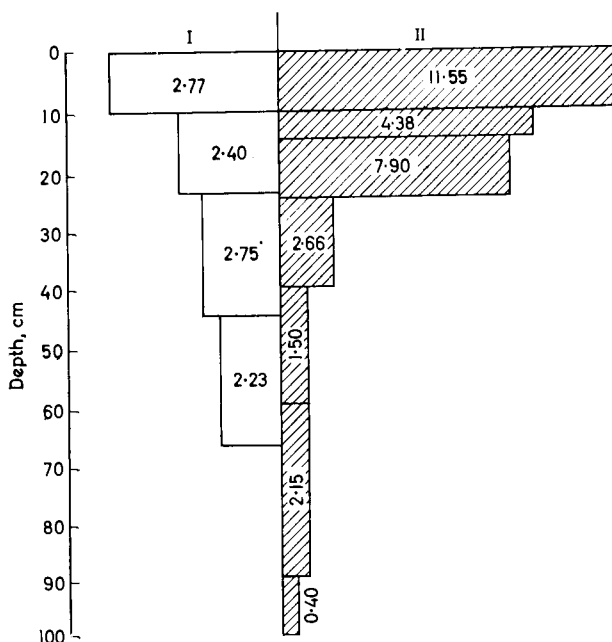


FIG. 71. The reserve of organic matter in krasnozem of Chakva.

I. Roots; II. Humus. Total amount of roots per sq m of the soil profile—10.15 kg, of which coarse roots amount to 2.94 kg; total amount of humus per sq m—30.54 kg; for the 0-25 cm layer—23.83 kg.

The humus of krasnozems is clearly unstable; the amount of substances extractable during decalcification is up to 20 per cent of the total amount of humus. Apparently, these substances are intermediate products of organic matter decomposition and also, partly, products of the acid hydrolysis of humus substances. Humus substances occur in krasnozem either in a free state or combined with sesquioxides.

Data obtained by Bel'chikova (1951) and also by Nyu Tsziven' (1961) on the humus content and its composition in krasnozems of Chavka are given in Table 75. Comparable results can be found in the work of Bziava (1949b) and Sabashvili (1954). Also in Table 75 are data on krasnozems

TABLE 75. CONTENT AND COMPOSITION OF HUMUS FROM KRASNOZEMS AND LATERITIC SOILS UNDER FOREST VEGETATION

Soil and locality	Depth of sampling (cm)	Organic C %	N %	C:N ratio	Carbon of humus fractions as % of total soil organic C				Author
					humic acids	fulvic acids	humic acid / fulvic acid ratio	Mobile forms of humic acids	
Krasnozem overlying andesite-basalt, Chakva	0-15	7.01	0.39	17.9	23.5	28.5	0.83	97.0	Bel'chikova (1951)
	35-40	1.15	0.06	19.2	5.2	22.6	0.23	100.0	Nyu Tszzi-Ven' (1961)
	0-20	5.36	0.37	14.5	14.1	21.7	0.66	100.0	Nyu Tszzi-Ven' (1961)
	20-40	1.25	0.07	17.9	3.2	24.0	0.13	100.0	Nyu Tszzi-Ven' (1961)
Krasnozem overlying gneiss, Yun'nan' Province, Chinese People's Republic	0-10	1.54	0.15	10.3	12.3	30.5	0.40	79.0	Nyu Tszzi-Ven' (1961)
	50-60	0.55	0.06	9.2	none	27.3	—	—	Nyu Tszzi-Ven' (1961)
Mountain lateritic humus soil overlying gneiss, Viet-Nam Democratic Republic	12-22	6.32	0.45	14.0	17.9	31.7	0.57	100.0	Nyu Tszzi-Ven' (1961)
	40-50	0.97	0.07	13.9	9.3	29.9	0.31	—	Nyu Tszzi-Ven' (1961)
Lateritic soil overlying basalt, Viet-Nam Democratic Republic	0-20	2.25	0.23	9.8	6.2	34.7	0.18	100.0	Nyu Tszzi-Ven' (1961)
	20-30	1.59	0.15	10.6	—	—	—	—	Nyu Tszzi-Ven' (1961)
	40-50	1.16	0.10	11.6	—	—	—	—	Nyu Tszzi-Ven' (1961)

from the province Yun'nan' of the Chinese People's Republic. The humus of this soil differs from the humus of the Chakva krasnozems in having a higher nitrogen content, shown by a C:N ratio of 9-10. The ratio of the humic acid groups to the fulvic acid groups is similar in both soils. The table also includes data for lateritic soils from the Vietnam Democratic Republic; these are in general similar to those for krasnozems. In spite of wide variations in the carbon and nitrogen contents, fulvic acids rather than humic acids predominate in the composition of humus from lateritic soils. Humic acids are represented by the fractions extracted from non-decalcified soil by a single treatment with 0.1 N NaOH. Tu Men-chao (1961), studying the humus of a lateritic concretionary soil under grass vegetation, obtained similar results: the humic acid carbon/fulvic acid carbon ratios in the profile of this soil varied from 0.42 to 0.36 and 0.27.

The conditions of soil formation in krasnozems and lateritic soils favour the production of humic acids with weakly expressed aromatic carbon nets; this is indicated by their low optical density (Table 76). In

TABLE 76. OPTICAL DENSITY (D) OF HUMIC ACIDS FROM KRASNOZEMS AND LATERITIC SOILS

Soil and locality	Depth of sampling (cm)	Optical density at wavelength $m\mu$						
		726	665	619	574	533	496	465
Krasnozems overlying andesite-basalt, Chakva	0-15	0.17	0.31	0.44	0.60	0.78	1.07	1.29
	0-20	0.11	0.21	0.34	0.49	0.68	0.88	1.11
Krasnozems overlying gneiss, Yuan'-Nan' Province, Chinese People's Republic	0-10	0.20	0.37	0.58	0.80	1.07	1.42	1.75
Mountain lateritic humus soil overlying gneiss, Viet-Nam Democratic Republic	12-22	0.15	0.26	0.38	0.58	0.79	1.05	1.33
	40-50	0.08	0.19	0.30	0.49	0.63	0.91	1.14
Lateritic soil overlying basalt, Viet-Nam Democratic Republic	0-20	0.15	0.23	0.38	0.60	0.85	1.13	1.53

agreement with this conclusion, humic acids in these soils are very resistant to the precipitating action of electrolytes, indicating that their molecules contain a preponderance of side radicals with hydrophilic groups (Table 77).

TABLE 77. THRESHOLD OF COAGULATION (PRECIPITATION) OF HUMIC ACIDS FROM KRASNOZEMS AND LATERITIC SOILS

Soil and locality	Depth of sampling (cm)	Beginning of coagulation		Complete coagulation		Author
		time (hrs)	CaCl ₂ , m eq per litre humate solution	time (hrs)	CaCl ₂ , m eq per litre humate solution	
Krasnozem overlying andesite-basalt, Chakva	0-15	—	—	4	13	Bel'chikova (1951)
	0-20	immediate	20	4	40	Nyu Tszi-Ven' (1961)
Krasnozem overlying gneiss, Yun'nan' Province, Chinese People's Republic	0-10	„	7	4	20	Nyu Tszi-Ven' (1961)
Mountain lateritic humus soil overlying gneiss, Viet-Nam Democratic Republic	12-22	„	10	4	30	Nyu Tszi-Ven' (1961)
	40-50	„	40	4	absent	
Lateritic soil overlying basalt, Viet-Nam Democratic Republic	0-20	„	15	4	40	Nyu Tszi-Ven' (1961)

It is interesting that the young volcanic soils of Japan are very similar in humus composition to soils of the tropical zone (Kanno, 1962).

Because of the high fulvic acid content in the humus of krasnozems and the peculiar nature of the humic acids (which are similar to fulvic acids in a number of properties), the humus is active in destroying the mineral part of the soil, in forming organo-mineral compounds and in causing their movement in the soil profile. Chelate-type iron-humus com-

plexes have been detected in krasnozems by Titova. The soil was extracted once with 0.1 N NaF ($\text{pH} = 7.0$) and after electrophoresis of the extract, complexes of such a nature were revealed very distinctly on the electrophoretograms. The carbon of the complexes comprised about 12 per cent of the total soil carbon (Titova, 1962).

Humus of mountain soils

The conditions of soil formation that determine the nature and content of humus are very diverse in soils of mountain regions. Investigations of this problem are not numerous but nevertheless deserve attention; a brief account of this work is given here.

Assing (1960) investigated a number of soils ranging from high mountain alpine and sub-alpine soils to serozems of the foothill plain in Northern Tyan'-Shan. She discovered that distinct general principles govern the changes in humus content and its composition, and these may be formulated as follows.

1. The soil humus content gradually increases on passing from the foothill arid light serozems to the high alpine meadow soils.

2. All the soils are characterized by a narrow C : N ratio, indicating the high nitrogen content of the humus. This is also true for the mountain dark chestnut soil and the mountain ordinary chernozem, and distinguishes them from the analogous soils in the plains.

3. On passing from mountain chernozems to mountain-forest and mountain-meadow soils, the humic acid/fulvic acid ratio alters towards preponderance of fulvic acids, while at the same time the soils have high humus and humic acid contents; this is not observed with the soils of the plains.

4. A large part of the humic acid group of substances is extracted by a single treatment of the non-decalcified soil with 0.1 N NaOH. This fraction apparently represents the free forms of humic acids; a high content of this fraction in the humus composition indicates great mobility of the humic acids (Table 78).

The nature of the organic matter in mountain soils of Tadzhikistan has been studied by Ilovaiskaya (1959). Characteristic features common to most of the soils studied by her are as follows.

1. The nitrogen content of the humus is high relative to carbon.

2. A fairly high proportion of the humic acids is extracted from the non-decalcified soil by a single treatment with 0.1 N NaOH.

3. Fulvic acids predominate over humic acids; a direct relationship is not found between the amount of humic acids and the total

humus content. The highest fulvic acid contents were recorded in the humus of mountain soils with a high humus content that develop under conditions of increased moisture and relatively low temperatures (Table 79).

These conclusions by Ilovaiskaya about the nature of the humus from the high-mountain soils of Tadzhikistan agree with Assing's results discussed earlier; however the rates of humus accumulation and the contents of humic and fulvic acids differ substantially (see Tables 78 and 79). Ilovaiskaya has established that humic acids from mountain-meadow and mountain-forest soils have a low optical density, which indicates that the net of aromatic carbon in their molecules is only weakly condensed. In addition these humic acids are extremely stable towards electrolytes. It appears to us that these properties of the soils may be due to large amounts of newly-formed humic acids being present in the humus.

Degtyareva (1960) has investigated the humus content and composition of the mountain-meadow and mountain-meadow-steppe soils in Azerbaidzhan (Kadabek region). The soils have a very high humus content which reaches 15–20 per cent in the upper 0–10 (20) cm horizon of the mountain-meadow soils and 10–12 per cent in the uneroded mountain-meadow-steppe soils. In the humus composition humic acid carbon varies from 20 to 30 per cent of the total soil carbon, and fulvic acid carbon from 25 to 35 per cent; the humic acid/fulvic acid ratio is 0.60–0.80 for the mountain-meadow soils and close to unity for the mountain-meadow-steppe soils. These features, and also a high mobility of the humic acids noted by the authors, are apparently common in the mountain-meadow and meadow-steppe soils.

Data characterizing the nature of humus in the brown forest soils of the Caucasus and Cis-Caucasus are given by Zonn (1950), Rubilin (1956) and Romashkevich, 1959; some of these data are quoted in Table 80.

Judging from these results, the characteristics noted earlier in mountain-meadow soils are retained in the humus of brown mountain-forest soils, namely, a high nitrogen content in the humus, a preponderance of fulvic acids over humic acids in the humus composition and a high proportion of the humic acids extracted by a single treatment of the non-decalcified soil with 0.1 N NaOH. Romashkevich reported that the humic acids had a fairly low optical density and a high stability to the precipitating action of electrolytes. However, attempts to reveal substantial differences in the humus composition of brown forest soils according to their vertical distribution have not been successful.

TABLE 79. CONTENT AND COMPOSITION OF HUMUS FROM HIGH MOUNTAIN SOILS OF TADZHIKISTAN (Ilovaiskaya, 1959)

Soil, locality and absolute altitude, metres	Depth of sampling (cm)	Organic C %	N %	C:N ratio	Carbon of humus fractions as % of total soil organic C			
					humic acids	fulvic acids	humic acid / fulvic acid ratio	Mobile forms of humic acids
High mountain forest soil under juniper, Turkestan ridge, 2500	10-30	3.87	0.476	8.1	13.5	51.4	0.26	14.8
Typical mountain-meadow soil, Peter the Great ridge, 3000	0-15	4.38	0.588	7.5	14.1	40.6	0.35	92.2
High mountain sod-meadow soil, Gissarsk ridge, 3380	0-20	2.88	0.476	6.0	12.9	54.0	0.24	30.2

TABLE 80. CONTENT AND COMPOSITION OF HUMUS FROM BROWN MOUNTAIN-FOREST SOILS OF CAUCASUS

Soil, land use, locality and absolute altitude, metres	Depth of sampling (cm)	Organic C %	N %	C:N ratio	Carbon of humus fractions as % of total soil organic C				Author
					humic acids	fulvic acids	humic acid/ fulvic acid ratio	Mobile forms of humic acids	
Brown forest soil under fir, North- West Caucasus, 1500 Podzolized brown forest soil under beech forest, North Osetiya	1-5	5.95	—	—	23.2	26.1	0.89	—	Zonn (1950)
	5-10 21-27	2.80 1.22	— —	— —	26.8 27.0	35.0 41.0	0.76 0.66	43.7 39.5	Rubilin (1956)
Brown forest soil under hornbeam- beech forest, foot hill area region Krasnodarsk, 250	0-10	3.77	0.43	8.77	18.7	25.4	0.73	54.6	Romashkevich (1959)
	7-17	2.56	0.25	10.24	20.2	24.6	0.82	62.4	Romashkevich (1959)
Brown forest soil under fir, high mountains, 1400	4-15	6.34	0.74	8.56	21.3	27.3	0.78	72.3	Romashkevich (1959)

TABLE 81. CONTENT AND COMPOSITION OF HUMUS FROM BROWN MOUNTAIN-FOREST SOILS OF CRIMEA (Dolgilevich, 1957, 1959, 1962)

Soil and land use	Depth of sampling (cm)	Organic C %	N %	C:N ratio	Carbon of humus fractions as % of total soil organic C			
					humic acids	fulvic acids	humic acid/fulvic acid ratio	Mobile forms of humic acids
Brown mountain-forest soil under beech forest overlying mixed deluvium of shaley clay and sandstone	1.5-11	3.95	0.36	10.9	20.5	21.7	0.9	72.0
	11-27	1.16	0.15	7.7	14.6	31.9	0.5	43.0
	27-45	1.00	0.11	9.0	15.0	20.0	0.7	—
Brown mountain-forest soil under beech forest overlying deluvium of limestone	1.5-6.5	3.58	0.29	12.3	22.0	25.7	0.9	45.0
	6.5-22	1.75	0.20	8.8	17.7	17.7	1.0	none
	22-43	1.45	0.14	10.4	17.9	22.8	0.8	—

Dolgilevich (1957, 1959, 1962) investigated the nature of the humus in brown-mountain-forest soils of the Crimea. These soils, which overlie various parent rocks at a height of 680 metres above sea level, have a low humus content except in the upper horizons; the C:N ratio is somewhat wider than in the analogous soils of the Caucasus. The humic acid carbon/fulvic acid carbon ratio is slightly less than unity, and the variations in this ratio in individual instances do not conform to any general pattern. As with other mountain soils, half or more of the total humic acids is extracted from a non-decalcified soil by a single treatment with 0.1 N NaOH (Table 81).

Ponomareva (1962) has formulated similar principles for the humus of brown forest soils. She considers that in these soils brown humic acids, which have similar functions to fulvic acids, take part in the soil-forming process; fulvic acids are neutralized by Ca, Mg and K, which are present in the leaf fall from oak and hornbeam forests.

From this survey of work on the humus of mountain soils in Central Asia, the Caucasus and the Crimea, the following conclusions can be drawn. The humus of mountain soils is characterized by:

1. A high nitrogen content.
2. A predominance of newly-formed humic acids and fulvic acids in the humus composition.
3. The presence of mobile forms of humic acids.

However, the data at present available are insufficient for a comparison to be made over a wide geographical area.

CONCLUSIONS

In the present chapter, facts and considerations on the natural conditions of humus formation determining the amount, composition and nature of humus substances in the soil have been presented. From the example of a series of soils it was shown that the state of the organic part of the soil depends not on any one factor but on their combined effect.

The increasing amount of humus in the series of soils ranging from tundra, podzolic, gray forest soils and chernozem, which we investigated, is due to the change from a forest cover to grass vegetation, to the increasing number of micro-organisms, to their diversity and increasing biochemical activity and also to the conditions of moderate moisture.

The conditions in chernozems ensure that humification of plant material leads mainly to the formation of humic acids, and the high mineral colloid content favours the fixation of humus.

For chestnut and solonets soils, it was shown that the amount of humus decreases as a result of decreasing denseness of the plant cover—by the replacement of grass species by plants characteristic of dry steppe, and also as a result of the change in hydrothermal conditions, which shortens the period of microbiological activity. The decreasing exchange capacity of the mineral part of the soil and the presence of exchangeable sodium in chestnut soils, and particularly in solonetses limits the capacity for the fixation of humus substances in the soils of this series.

In this sequence, the brown soils of the arid steppe, and even more the takyr of the desert zone, which are practically devoid of higher vegetation, are the poorest in humus.

A separate place is occupied by serozems, where a sufficient amount of precipitation in the spring months (March and April and the beginning of May) and fairly high temperatures allow the luxurious development of ephemeral vegetation and microbiological activity; these assist the new formation and decomposition of humus substances.

Microbiological processes are particularly intense when serozems are irrigated.

The criteria for characterizing the nature of humic acids which we introduced—optical density of humate solutions and the coagulation-threshold values—revealed marked differences in humic acids of different soils, which explains the differing degree of participation in soil formation.

Thus, according to these criteria, the humic acids of northern podzolic soils (and partly of krasnozems) are closer to fulvic acids than to the humic acids of other soils (particularly chernozems). They are highly dispersed; with this is associated their high mobility, active participation in the decomposition of the mineral part of the soil and their inferior qualities as structure-forming agents.

On passing towards sod-podzolic soils and further, to chernozems, humic-acid molecules increase in complexity and are therefore less dispersed; they lose mobility and acquire the capacity for forming insoluble humates (Ca) and other stable forms of organo-mineral compounds. With this is associated their increasing participation in structure formation and their capacity for accumulation in the soil, most clearly expressed in chernozems.

An examination of the material discussed in this chapter shows that a moderate moisture regime, a neutral reaction and a fairly intense microbiological activity are the main factors favouring the formation of complex humic acids. Excess moisture, acid reaction and weak microbiological

activity suspend the formation of humus substances at the stage of fulvic acids and fulvic acid-like humic acids.

Fulvic acids predominate in the humus of serozems because both the new formation and decomposition of humus substances are very intense.

In the USSR, investigations on the nature of the humus of different soils have been considerably extended in recent years. However, even the latest investigations do not include the whole diversity of the soil cover of the USSR, some idea of which can be seen from Rozov's description included in this book; in this respect, the soil scientists of the USSR are faced with further studies, particularly of the humus of soils of little-investigated regions. Similar investigations developing Dokuchaev's ideas on the regular character of the process of humus formation are of importance in finding a solution to soil-genetic problems and are at the same time helpful in developing methods for the correct utilization of soils in agriculture and forestry.

It should be mentioned that the establishment of a relationship between the conditions of soil formation and the nature of the humus is attracting the attention of soil scientists outside the USSR: see, for instance, the work of Musierowicz, 1953, a, b, 1961 (Poland); Ehwald, 1956 (E. Germany); Stefanovits, 1949 (Hungary); Muresanu, 1960, 1961 (Rumania); Krastanov, 1962 (Bulgaria); Pelisek, 1962, Valek, 1962 (Czechoslovakia); Bogdanovic, 1962 (Yugoslavia); Albareda, 1955, 1960 (Spain); Kubiena, 1953, 1955, Scheffer, 1954 (W. Germany); Kosaka, 1953, 1963, Kanno, 1962 (Japan); Duchaufour and Dommergues, 1963; and others. Such work will undoubtedly help in studying the problems associated with the genesis and classification of soils.

CHAPTER 7

CHANGES IN SOIL ORGANIC MATTER UNDER DIFFERENT SOIL MANAGEMENT

THERE can be no doubt that it is important to study the pattern of the processes by which organic matter is accumulated and decomposed during soil cultivation; certain general aspects of the problem are fairly clear. It has been found, for instance, that under a perennial-grass cover natural and artificial fallows are enriched in humus as a result of the predominance of processes involving the new formation of humus substances over processes involving their decomposition. On the other hand, the humus content decreases with the ploughing-up of virgin lands and fallows and with the long-term continuous cultivation of annual crops, due to the fact that the decomposition of humus substances is not accompanied to a sufficient extent by the new formation of these substances.¹

In accordance with this, rational systems of agriculture which provide for the systematic replenishment of the organic-matter reserve of the soil should be worked out. The ways of bringing this about are diverse and depend primarily on the nature of the farm. We shall examine some examples. The experiments carried out in the USA merit attention. In many works on the problem of soil organic matter under irrigated and non-irrigated conditions in the USA the authors are unanimous in pointing out that the humus and nitrogen reserves of the soil decrease after a long period of cultivation of annuals in alternation with fallow. Furthermore, the most intensive decomposition of organic matter occurs under irrigated conditions.

We shall mention the work of Swanson and Latshaw (1919), Johnes and Yates (1924), Gainey, Sewell and Latshaw (1929), Lyon, Lyttleton (1929), Burgess (1929), Russell (1929), Salter and Green (1933), Bracken

¹ For a review of the literature on this problem, see: Waksman, S. A. (1936) *Humus. Origin, Chemical Composition and Importance in Nature*; Tyurin, I. V. (1937) *Soil Organic Matter*, Moscow; Russell, E. W. (1961) *Soil Conditions and Plant Growth*, 9th Edition, Longmans, Green and Co. Ltd., London.

and Greaves (1941), Smith, Wheeting and Vandecaveye (1946), Atkinson and Wright (1948), Lee Ching-Kwei and Bray (1949), Smith, Thompson *et al.* (1954), and others. Data showing the character of the organic-matter transformation in the soil with different land utilization are given by Jenny (1941) (see Fig. 72).

After observing the deleterious effect of a decrease in soil organic matter, these authors point out that the sowing of perennial grasses, green manur-

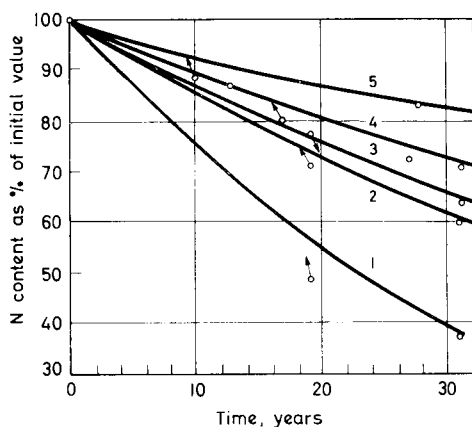


FIG. 72. The content of organic nitrogen with different land utilization (from Jenny's book *Factors of Soil Formation*; the data of Salter and Green on clay loam soil. Rotation since 1894).

1. Continuous maize; 2. Continuous wheat; 3. Continuous oats; 4. Five-course rotation: maize, oats, wheat, clover and timothy; 5. Three-course rotation: maize, wheat and clover.

ing and the application of farmyard manure are the most important measures for restoring soil fertility.

Bear (1950) considers that to maintain soil organic matter at a definite level, it is essential to apply $2\frac{1}{2}$ tons of farmyard manure per acre annually.

In these circumstances attempts are being made to utilize cereal straw for the replenishment of the organic-matter reserve of the soil. For better humification and to avoid the deleterious effect of straw on the plant due to temporary conversion of the mineral nitrogen into organic forms (this is usually observed during the decomposition of plant residues with low nitrogen content) combining this practice with the application of mineral nitrogen is recommended. However, data from the works of Smith, Wheeting and Vandecaveye (1946) which survey the results of long-term

experiments at the Washington State Experiment Station (on light sandy loams) do not support the use of this method.

Actually, although in some of the experimental treatments an increase in the percentage of humus with the application of straw and ammonium sulphate was demonstrated, it was very small and not consistent in the individual variants. The average grain yield in an 18-year experiment was found to be fairly similar in the individual variants; a decrease of about 2–4 bushels/acre or 14–20 per cent in the calculated value of the average yield for the second half of the experimental period (9 years) compared with that for the first 9 years was observed.

The problem of the balance of soil humus in agriculture has attracted attention in France (Barbier, 1943; Hénin and Dupuis, 1945). After calculating the amount of residues left behind by crops in a rotation and the corresponding amount of newly formed humus substances (with humification coefficient = 0.4), Hénin and Dupuis concluded that the new formation of humus substances from the plant residues did not compensate for the decomposition of soil humus. To cover this deficit an additional source of organic matter was necessary; according to these authors farmyard manure is of prime importance in this respect.

It should be noted that the possible supplementation of humus substances by the growing plants in the rotation was underrated. This was calculated from the amount of root residues left behind by the crops after harvest. However, new formation of humus substances also takes place during plant growth as a result of the dying-off and humification of rootlets and root hairs. The scale of this process is particularly large with perennial grasses under the conditions of a long growth period (examples will be examined in the section "The accumulation of root residues under perennial grasses" in this chapter). Therefore, with the systematic sowing of perennial grasses and their alternation with annual crops, the balance of organic matter is more favourable than Hénin and Dupuis imagined. However, there is, of course, no doubt about the importance of the systematic application of farmyard manure and other organic manures to the soil for reducing the deficit in the organic-matter balance in field rotations.

Information about the regime of organic matter in long-term experiments is of great interest. Summarizing results from the Broadbalk experiment at Rothamsted, Russell (1961) concluded that when uncultivated land is ploughed, a rapid decay of organic matter and loss of nitrogen occurs until a new level of organic matter is stabilized. Regular application of farmyard manure contributes to an increase in soil organic matter or decreases its loss.

The same conclusion was reached by Schmalfuss (1950) and Montulyak (1960) who summarized results from long-term experiments at Halle-Zaal (G.D.R.).

The need for a systematic replenishment of organic matter in the soil was pointed out by a number of German investigators (Scheffer, 1941, 1957; Laatsch, 1944, 1948; Springer, 1952, 1957; Sauerlandt and Groetzner, 1953; and others), who closely associated soil fertility with the manifold functions of humus (as a source of ash nutrients and carbon for plants and also as a reserve of various biotic substances). Accordingly, methods of enriching the soil in organic matter (the application of farmyard manure, peat, various composts, the sowing of grasses), in conjunction with the application of mineral fertilizers, are considered to be indispensable for obtaining high and consistent yields.

The hypothesis that a direct relationship exists between soil fertility and the presence of organic matter in the soil was accepted in Russia a long time ago. Accordingly, the importance of the replenishment of the humus reserve by means of organic manures and the sowing of annual and particularly perennial grasses (rapidly returning old cultivated land to a state of fallow) was noted by Izmail'skiĭ, Dokuchaev, Kostȳchev, Timiryazev and Williams.

However, with the great diversity of soil-climatic conditions in the Soviet Union the character of the cycles of accumulation/decomposition of organic matter is not everywhere the same. It is from this standpoint that we have attempted to analyse available data on the transformation of organic matter in cultivated soils under different soil-climatic conditions.

We have grouped relevant data into the following classes:

1. The decomposition of organic matter with the ploughing-up of virgin soils followed by a long period of cultivation of annual crops.
2. The accumulation of humus with the systematic application of farmyard manure.
3. The accumulation of humus in natural fallow.¹
4. The change of organic matter in the soil under ley rotations in various soil-climatic zones.
5. The change of organic matter with complex methods of soil cultivation.

The data available at the present time limit the examination of the problem to the following groups of soils: (a) soils of the southern part

¹ See footnote on p. 340.

of the sod-podzolic soil zone; (b) chernozems of the zone of variable moisture; (c) chernozems and chestnut soils of the zone of inadequate moisture; (d) irrigated serozems.

THE DECOMPOSITION OF ORGANIC MATTER RESULTING FROM PLOUGHING-UP VIRGIN SOILS AND LONG-TERM CULTIVATION OF ANNUAL CROPS

Sod-podzolic soils

We turn now to the experiment started in 1912 by Pryanishnikov on a sod-podzolic light loamy soil at the Timiryazev Academy. This experiment has been systematically investigated at the Academy and so the rate

TABLE 82. HUMUS AND NITROGEN CONTENTS OF A SOD-PODZOLIC LIGHT LOAMY SOIL IN THE LONG-TERM EXPERIMENT AT THE TIMIRYAZEV ACADEMY

Land	Humus, % of soil weight	Nitrogen, % of soil weight	Decrease in hu- mus content		Author
			% of soil weight	% of virgin land	
Virgin land	2.22-2.19	0.159	—	—	
Continuous fallow 13 years					
Unmanured	1.27	0.091	0.95	43	Drachev (1927)
Farmyard manure	2.14	0.125	0.08	9	Drachev (1927)
Continuous fallow 48 years					
Unmanured	1.05	—	1.14	52	Lykov(1961)
Farmyard manure	1.62	—	0.57	26	Egorov (1961)
Continuous rye 48 years					
Unmanured	1.55	—	0.64	29	Egorov (1961)
Farmyard manure	2.50	—	+0.31	+14	Egorov (1961)
Rotation, 48 years					
Unmanured	1.57	—	0.62	28	Egorov (1961)

of decomposition of the organic matter in the soil can be estimated for different types of land management.

The results in Table 82 show that when virgin land on a sod-podzolic soil is ploughed, there is at first a period of intense decomposition of the organic matter. After a period of 13 years continuous fallow, the humus and nitrogen contents had decreased by 43 per cent. Subsequently the process is stabilized, apparently because micro-organisms have used up the most easily available organic matter; during this 32-year period, humus in the fallowed soil decreased by only 9 per cent.

The presence of vegetation and also the regular application of farmyard manure almost halves the losses of humus, and when agricultural crops are grown after manuring, the humus content in the soil is maintained at the level originally found in the virgin land.

Therefore in spite of the fairly high rate at which organic matter decomposes in sod-podzolic soils (in the southern part of the taiga zone), a sufficiently high humus content can be maintained by agrotechnical methods.

We shall return below to the fixation of the organic matter of farmyard manure in soil and the simultaneous changes in the composition of humus.

Chernozem soils in zones of moderate and variable moisture

In reviewing literature on the decomposition of organic matter after the ploughing of virgin chernozems, we shall deal first with podzolized chernozem. Lazarev (1936) determined the content of humus and nitrogen in soils of the Shatilovskaya Station under a 3-course rotation since 1909. At the time of sampling this rotation was 23 years old. The controls were virgin areas bordering the rotation fields. Data on the contents of humus and nitrogen in these soils are given in Table 83.

In the 3-course rotation over a period of 23 years a large amount of humus was decomposed, representing 1–2 per cent of the soil weight, which calculated for 1 ha of the arable layer amounts to 25–50 tons. In relation to the total humus reserve of the arable layer, this represents 16–23 per cent.

For comparison with sod-podzolic soil the data obtained for ordinary chernozem soil of the Voronezh Experimental Station are of great interest (Table 84).

During a 10–12-year period of continuous fallowing the soil lost an enormous amount of humus, representing 1.55–2.28 per cent of the soil weight, or approximately 45–60 tons/ha; this constituted 19–27 per cent

TABLE 83. HUMUS AND NITROGEN CONTENTS OF THE 2-12 CM LAYER OF PODZOLIZED CHERNOZEM (Lazarev, 1936)

Utilization	C _{org}	N	Hu- mus	Humus decomposed	
				% of soil weight	% in relation to virgin soil
Virgin land	5.91	0.406	10.17	—	—
Fallow	4.74	0.307	8.15	2.02	20.0
Virgin land	5.24	0.325	9.00	—	—
Rye	4.02	0.235	6.91	2.09	23.0
Virgin land	4.21	0.327	7.24	—	—
Oats	3.55	0.253	6.10	1.14	16.0

TABLE 84. HUMUS CONTENT OF THE 0-20 CM LAYER OF ORDINARY CHERNOZEM (Ivanov, 1938)

Utilization	Hu- mus	Humus decomposed	
		% of soil weight	% in relation to natural fallow
Virgin land	8.40	—	—
Continuous 10-yr fallow	6.85	1.55	19
Virgin land	8.48	—	—
Continuous 12-yr fallow	6.20	2.28	27

of the total amount of humus in the virgin land. Thus, the absolute amount of humus decomposed under continuous fallowing on ordinary chernozem considerably exceeded the amount decomposed under similar conditions in sod-podzolic soil. However, in relation to the total amount of humus in the cultivated layer the decomposition proceeds more economically in ordinary chernozem than in sod-podzolic soil.

Data on the humus content of ordinary chernozem of the Kamennaya steppe (Voronezh region) are of considerable interest. After comparing the humus content with different utilization of this soil, Lazarev (1936) and Chizhevskii (1938) showed that there was less humus under various crops than under natural fallow of long duration.

In our laboratory Bel'chikova determined the humus reserve of soil under cut steppe of the Dokuchaev Institute of Agriculture (Kamennaya steppe) and compared the value obtained with that obtained for cultivated

soil, not included in a ley rotation, of the collective farm Vysokiĭ. To obtain an accurate calculation of the humus reserve Bel'chikova took into account the depth of the layers and the volume weight of the soil. Comparative data are given in Tables 85 and 86.

TABLE 85. HUMUS RESERVE OF SOIL UNDER CUT STEPPE CALCULATION
FOR AN AREA OF 1 m²

Depth of horizon (cm)		Volume weight of soil	Weight of soil layer (kg)	% content		Amount of humus (kg)
				C _{org}	hu- mus	
A ₀	0-6	0.72	43.2	7.54	12.97	5.60
A ₁	6-20	0.96	134.4	5.75	9.89	13.29
A ₂	20-42	1.02	224.4	4.30	7.40	16.60
B ₁	42-57	1.15	172.5	2.84	4.88	8.41
B ₂	57-75	1.26	226.8	1.94	3.33	7.55
B ₃	75-100	1.58	395.0	0.74	1.27	5.02
Total:						56.47

TABLE 86. HUMUS CONTENT OF PLOUGHED SOIL OF THE COLLECTIVE FARM
"VYSOKII"; CALCULATION FOR AN AREA OF 1 m²

Depth of horizon (cm)		Volume weight of soil	Weight of soil layer (kg)	% content		Amount of humus (kg)
				C _{org}	hu- mus	
A ₀	0-22	1.00	220	4.49	7.72	16.98
A ₁	22-37	1.10	165	3.72	6.29	10.38
A ₂	37-47	1.23	123	2.98	5.13	6.31
B ₁	47-60	1.32	171	1.55	2.67	4.58
B ₂	60-80	1.37	274	0.78	1.34	3.67
	80-90	1.51	151	0.52	0.89	1.34
B ₃	90-100	1.52	152	0.50	0.86	1.31
Total:						44.57

When the condition of these soils was initially identical, a long period of continuous cultivation of annual crops in alternation with fallow resulted

in a considerable loss of humus, amounting to approximately 80 tons/ha. This represented 22–23 per cent of the total humus reserve.

From an examination of data on the intensity of humus decomposition after the ploughing-up of virgin podzolized and ordinary chernozem of the variable-moisture zone, a fairly definite regularity is observed: with a long period of cultivation of annual crops in alternation with fallow, or with continuous fallowing, an intensive decomposition of humus is observed, amounting, in the arable layer alone, to several dozen tons/ha.

In absolute values, this amount in chernozems is considerably greater than the amount occurring in sod-podzolic soil, but a comparison with the total reserve indicates that the decomposition of humus proceeds more economically in chernozem than in sod-podzolic soil.

Chernozem and chestnut soils in zones of inadequate moisture

On passing towards soils of drier regions a clear retardation in the decomposition of humus is observed after the ploughing of virgin lands for annual crops in alternation with fallow. This regularity was apparent from the work of Vinokurov (1936) in Western Siberia, Khvorov and Onokhova (1939) in the Kustanaisk region, Orlovskii (1935) in the Ural' region, and Rubinstein (1959) in Kazakhstan.

Some data from the work of Khvorov and Onokhova are presented in Table 87.

A similar trend in the values characterizing the intensity of humus decomposition was obtained by Khvorov and Onokhova for chestnut soil (Table 88).

TABLE 87. HUMUS CONTENT OF THE 0–18 CM LAYER IN MEDIUM-LOAM CHERNOZEM (Khvorov and Onokhova, 1939)

Period of cultivation	Humus content as % of air-dry soil		Humus decomposed	
	in virgin land	in arable land	% of soil weight	% in relation to virgin land
2 yrs after ploughing virgin land	8.50	8.30	0.20	2.4
4 yrs after ploughing virgin land	8.50	8.13	0.37	4.4
10 yrs after ploughing virgin land	8.19	7.46	0.67	8.3
28 yrs after ploughing virgin land	7.74	6.53	1.21	15.7

TABLE 88. HUMUS CONTENT OF THE 0-18 CM LAYER IN CHESTNUT SOIL
(Khvorov and Onokhova, 1939)

Period of cultivation	Humus content as % of air-dry soil		Humus decomposed	
	in virgin land	in arable land	% of soil weight	% in relation to virgin land
2-3 yrs after ploughing virgin land	4.77	4.64	0.13	2.6
6 yrs after ploughing virgin land	4.74	4.47	0.27	5.7
10 yrs after ploughing virgin land	4.52	4.19	0.33	7.4
23 yrs after ploughing virgin land	5.01	4.36	0.65	13.0
30 yrs after ploughing virgin land	5.10	3.92	1.18	23.1

We shall turn now to the data of Khvorov and Onokhova for a 10-year cultivated medium-loam chernozem in order to make a comparison with the previously considered soils; this soil lost 0.6 per cent of its humus, or approximately 20 tons/ha. In relation to virgin land this amounted to only 8.3 per cent. In a 10-year cultivated chestnut soil the amount of humus decomposed was 7.4 per cent of the amount of humus of virgin land. In a 10-year period of continuous fallow on ordinary chernozem of the Voronezh Experimental Station the amount of decomposed humus was 1.55 per cent (about 35 tons/ha), which constituted 19 per cent of the amount of humus in relation to virgin land. It will be remembered that for continuous fallow in the sod-podzolic zone, the amount of humus decomposed in a 13-year period was 43 per cent relative to the amount of humus in the virgin land.

One should bear in mind that in the soils studied by Khvorov and Onokhova some replenishment of humus occurred due to the humification of the root residues of annual crops, but the latter, as is well known, are only a limited source of humus substances, and therefore the new formation of humus could not in this case be the cause of such clear differences in the humus content. Furthermore, in these experiments the crops were alternated with fallow.

The most likely cause of the observed differences is the retarded humification of organic matter in dry regions characterized by a moisture deficit, which reduces the intensity of biological activity during the summer period of high temperatures. Orlovskii (1935), in investigations at the Uralsk Experimental Station, obtained similar data (Table 89).

TABLE 89. PERCENTAGE CONTENTS OF HUMUS AND NITROGEN OF THE 0-18 CM LAYER IN CHESTNUT SOILS (Orlovskii, 1935)

Soils and utilization	Hu- mus	C _{org}	N	Decomposed humus	
				% of soil weight	% relative to virgin land
<i>Festuca-Stipa</i> , virgin land	5.44	3.16	—	—	—
Arable land (12 yrs ploughing)	4.94	2.87	—	0.50	9.0
<i>Carex</i> turf, virgin land	4.47	2.60	0.25	—	—
Arable land (5 yrs ploughing)	4.28	2.49	0.20	0.19	4.0
<i>Festuca-Stipa</i> , virgin land	2.57	1.49	0.18	—	—
Arable land (6 yrs ploughing)	2.37	1.37	0.16	0.20	8.0

In the works of the authors just mentioned above data are given on the decomposition of humus and nitrogen both for long and short periods (2-6 years) after the ploughing of virgin land. In such cases, the decomposition of humus amounted to 0.2-0.4 per cent of the soil weight or, in other words, to 4-5 per cent of the total humus content. The order of magnitude of these values is undoubtedly not great, as can be seen from a comparison with the humus losses in the zone of irrigated serozems, which indicates the opposite condition—a vigorous decomposition of organic matter.

Irrigated serozems

There is a fairly extensive literature available on the question of the decomposition of humus following the ploughing of virgin serozems for irrigated crops. These works indicate an extremely rapid decomposition of organic matter attributable to the high intensity of biological processes in irrigated serozems. Particularly favourable conditions for the decomposition of organic matter occur in soils under cotton receiving repeated irrigation and periodic loosening of the soil during the growth period (May-August). Consequently, after the reclamation of virgin soils for cotton, the decomposition of organic matter leads to a rapid decrease in nutrients and deterioration of soil structure and eventually to a considerable decrease in soil fertility.

Some idea of the intensity of decomposition of humus and nitrogen can be found in the work of Sinyagin (1939), who studied this process in various serozems with the mechanical composition of heavy loess-like loam. Unfortunately, no data on the duration of utilization of the virgin lands

were given so that it is not clear in which period the losses of humus and nitrogen occurred.

Comprehensive studies on the decomposition of organic matter in serozems were carried out by Gel'tser and co-workers.

According to Gel'tser and Lasukova (1934), virgin soil, after ploughing for cotton for a period of 3–7 years, loses about one-half of its total reserve of organic carbon, i.e. carbon of humus and plant residues (Table 90).

TABLE 90. ORGANIC CARBON AND NITROGEN CONTENTS OF THE 0–20 CM LAYER OF LIGHT SEROZEM (Gel'tser and Lasukova, 1934)

Investigated soils	% content		Decomposed organic C	
	C _{org}	N	% of soil weight	% of control
I. Virgin land:	0.78	0.097	—	—
Cotton—1st year after ploughing	0.60	0.086	0.18	23.0
2nd year after ploughing	0.48	0.076	0.30	38.0
3rd year after ploughing	0.37	0.059	0.41	50.0
II. Virgin land:	1.16	0.106	—	—
Cotton—3rd year after ploughing	0.77	0.111	0.39	34.0
7th year after ploughing	0.56	0.095	0.60	52.0

The rapid decomposition of organic matter in serozem is apparent from the experiments of Gel'tser and Lasukova (1934) on the determination of "soil respiration" under optimum temperature and moisture conditions (Table 91).

TABLE 91. PRODUCTION OF CO₂ IN LIGHT SEROZEM (Gel'tser and Lasukova, 1934)

Amount of CO ₂	Virgin land	Cotton after ploughing virgin land		
		1st yr	2nd yr	3rd yr
In mg per kg soil	181.7	110.0	66.0	59.4
As % in relation to virgin land	100	60.0	36.0	33.0

After the ploughing of virgin land for cotton, the reserve of easily-mineralized organic matter decreased by 40 per cent in the first year and

by a further 27 per cent during the next two years. As a result, after three years the amount of organic matter decreased to 33 per cent of its content in the virgin land.

An intensive decomposition of organic matter was also demonstrated by Gel'tser and Lasukova (1934) for typical serozem of heavier texture at the Ak-Kavak Experimental Station.

Our investigations (Kononova and Lagunova, 1940), in which we calculated the humus content in kg per sq m taking into account the volume weight of the soil and the thickness of the layers, also give an idea of the extent of humus decomposition during long continuous cultivation of cotton on virgin land.

The data given in Table 92 show that for a 10-year period of continuous cotton on virgin land, 53 per cent of the total reserve of humus was decomposed.

TABLE 92. ORGANIC CARBON, NITROGEN AND HUMUS CONTENTS OF LIGHT SEROZEM (Kononova and Lagunova, 1940)

Soils and utilization	Volume weight of soil	Weight of layer (kg)	C _{org}	N	Humus	Humus of 0-15 cm layer (kg)
Virgin land:						
0-10 cm layer	1.23	123	1.28	0.14	2.20	3.22
10-25 cm layer	1.23	185	0.48	0.07	0.83	
Cotton, continuous cultivation for 10 yrs after ploughing virgin land:						
0-15 cm layer	1.41	213	0.41	0.06	0.71	1.51

An indication of the intensive mineralization of nitrogen-containing organic compounds under irrigated conditions following the ploughing of virgin serozems is the sharp decrease in the nitrifying capacity.

To illustrate this we shall present our data. The determination of the nitrifying capacity was carried out in two variants: (1) without the addition of nitrogen and (2) with the addition of nitrogen in the form of $(\text{NH}_4)_2\text{SO}_4$. In both cases the temperature and moisture conditions of the soil were optimal. The first variant indicates the presence of easily mineralized organic nitrogen-containing compounds in the soil; the second, the potential

activity of nitrifying organisms in relation to their capacity for oxidizing NH_4 -nitrogen to nitrates (Table 93).

TABLE 93. NITRIFYING CAPACITY OF LIGHT SEROZEM (Kononova, 1930)

Soils and utilization	$\text{NO}_3\text{-N}$ formed after 20 days from soil nitrogen		$\text{NO}_3\text{-N}$ formed after 20 days from added $(\text{NH}_4)_2\text{SO}_4$	
	mg per kg soil	% in relation to virgin land	mg per kg soil	% in relation to virgin land
Newly ploughed virgin land	22.0	100	95.8	100
Cotton – 1st year after ploughing virgin land	13.60	61	102.6	107
Cotton – 2nd year after ploughing virgin land	11.20	51	180.8	188
Cotton – 4th year after ploughing virgin land	10.40	43	204.0	213

TABLE 94. HUMUS AND NITROGEN CONTENTS OF SEROZEMS (Belyakova, 1947)

Utilization and depth of layer (cm)	Humus		Nitrogen	
	% of weight of soil	% in relation to virgin land	% of weight of soil	% in relation to virgin land
Virgin land:				
0-15	3.10	100	0.155	100
15-30	2.70	100	0.135	100
Cotton-1st year after ploughing the virgin land:				
0-15	2.86	92.3	0.147	94.8
15-30	2.80	100	0.140	103.7
2 years after:				
0-15	2.01	65.0	0.101	65.0
15-30	1.78	66.0	0.089	66.0
2 years after:				
0-15	1.67	54.0	0.087	56.1
15-30	1.58	55.0	0.082	60.7
5 years after:				
0-15	1.16	37.4	0.056	37.4
15-30	1.24	46.0	0.066	49.0

The data presented in Table 93 indicate that after the ploughing of virgin land the reserve of easily mineralized nitrogen decreases rapidly so that by the 4th year, the nitrifying capacity with respect to soil nitrogen amounts to 43 per cent of that occurring in recently ploughed virgin land.

At the same time the activity of nitrifying micro-organisms increases with the cultivation of virgin land. This can be seen from the intensity of $(\text{NH}_4)_2\text{SO}_4$ oxidation, which, under cotton of the 4th year, was more than twice the intensity in virgin land.

Finally, we come to the work of Belyakova (1947) in connexion with irrigated serozems. In mechanical composition the soils were clayey loams. Some of Belyakova's data indicating the highly intensive decomposition of humus and nitrogen in this soil are presented in Table 94.

Thus, all the works examined by us are unanimous in pointing out the high intensity of decomposition and mineralization of organic matter in irrigated serozems. It is of very great importance that with continuous cotton cultivation, even over a relatively short period of 3–5 years, virgin serozems acquire the conditions of old-cultivated land. As we shall see later, a similar phenomenon is also observed after the ploughing of fields under perennial grasses.

CONCLUSIONS

The following patterns can be seen from a survey of the literature on the decomposition of organic matter after the ploughing of virgin lands and fallows.

With the ploughing of virgin lands and long-fallowed land and their continuous utilization for annual cereals and root crops, the ratio between the new formation and the decomposition of humus substances is altered in the direction of a predominance of the latter. As a result the soils become poorer in humus.

For various groups of soils, the following specific features characterizing the rate of this process can be noted:

1. The decomposition of humus and nitrogen-containing organic compounds occurs with greatest intensity in irrigated serozems under cotton, where about one-half of the total reserve of humus is decomposed during the first 3–5 years.
2. Apparently the decomposition of organic matter also proceeds fairly intensively after the ploughing of virgin lands and long-fallowed land in soils of the southern part of the sod-podzolic soil zone.
3. It was established fairly definitely that the decomposition of humus after the ploughing of virgin lands and long-fallowed land proceeded at a

reduced rate in chernozems and chestnut soils with inadequate moisture. Thus, the amount of humus decomposed in a 10-year period from the time of ploughing of the virgin land was not more than 7–9 per cent of the total amount of humus and in the first 3–5 years was approximately 3–5 per cent.

4. The intensity of humus decomposition after the ploughing of virgin chernozem of the zone of moderate moisture (podzolized chernozem) and the zone of variable moisture (ordinary chernozem) is somewhere intermediate between that of irrigated serozems and sod-podzolic soils on the one hand and soils of the zone of inadequate moisture on the other. The absolute losses of humus in this group of soils are very high although in relation to the total humus reserve they are clearly smaller than in soils of the first group.

In examining data characterizing the intensity of humus decomposition following the ploughing of virgin soils and long-fallowed land, we shall have to limit ourselves to changes in the total amount of humus and nitrogen, as only isolated data exist on the changes in the composition of the humus. It seems that at first easily mobilized organic substances of non-specific nature are decomposed, although there are indications of the decomposition of strictly humus substances, particularly humic acids. This follows from the work of Dubov (1932) showing that in a 13-year period of cultivation of the virgin land there was a decrease, not only in the absolute amount of humic acids, but also in their relative content in the composition of the humus (Table 95).

Similar results were obtained by Bel'chikova for ordinary chernozem of the Kamennaya Steppe during a determination of the composition of the humus of uncut steppe and intensively cultivated soil (Table 96).

TABLE 95. CONTENT AND COMPOSITION OF HUMUS OF THE 0–10 CM LAYER OF HUMIC-CARBONATE LOAM OF THE BAYANDAISK EXPERIMENTAL FIELD (Dubov, 1932)

Utilization	Total humus (%)		Total nitrogen (%)		Humic acids (%)	
	of soil weight	of control	of soil weight	of control	of soil weight	of total humus
Virgin land	6.68	100	0.38	100	2.20	31.9
3-course rotation	4.96	72	0.26	71	1.30	26.2
Continuous oats	5.10	74	0.27	73	1.30	25.4
Continuous rye	5.08	74	0.28	74	1.24	24.3
Continuous fallow	4.64	67	0.25	68	1.17	25.2

TABLE 96. COMPOSITION OF HUMUS OF THE 0–20 CM LAYER OF HEAVY-LOAM ORDINARY CHERNOZEM OF THE KAMENNAYA STEPPE (Bel'chikova, 1949)

Soils	C _{org} (%)	Humus (%)	In composition of humus		Humic acid/fulvic acid ratio
			humic acids	fulvic acids	
Long-term fallow†	6.63	11.40	$\frac{3.19^*}{48.1}$	$\frac{1.13^*}{17.0}$	2.8
Intensively cultivated soil	4.38	7.58	$\frac{1.81^*}{41.3}$	$\frac{0.90^*}{20.8}$	2.0

* Top row of figures indicates the carbon content of humic and fulvic acids in relation to the soil weight; the lower row indicates their percentage content in the composition of humus.

† *Translators' note:* this is a translation of the Russian term *mnogoletnyaya zalezh'* used for land which has not been cultivated for many years, during which time perennial plants, mainly grasses, have become established.

The decomposition of humus following the ploughing of virgin lands and long-fallowed land and with continuous cultivation of annual crops results in a marked deterioration of the most important soil characteristics—nutrient reserves and soil structure—even when the decomposition of organic matter proceeds slowly and the absolute losses of humus are not very great.

Therefore, even at a relatively low rate of organic-matter decomposition in the soil, the need for replenishing the reserves of newly formed (active) humus is still just as great.

FARMYARD MANURE AS A SOURCE OF HUMUS IN THE SOIL

The importance of farmyard manure for increasing soil fertility has been demonstrated over many centuries of agricultural practice, but whether it should be regarded solely as a source of nutrients, or, at the same time, as a source of humus is still not quite clear.

According to some work, farmyard manure considerably enriches the soil in humus. Thus, Drachev (1927) points out that the systematic application of farmyard manure to a fallow for a period of 13 years increased the humus content of the soil by 0.87 per cent. From calculations presented earlier in this chapter, this value represents approximately 50 per cent of the total amount of farmyard manure applied during the whole experi-

mental period (53 tons/ha). Hence, in this experiment about half of the total amount of farmyard manure was mineralized and the other half remained in the soil as humus.

Tyulin (1939) demonstrated a still greater increase in humus with the systematic application of farmyard manure on podzolic soil of the Smolensk Experimental Station. In this experiment, 120 tons/ha were applied during a period of 12 years; this was equivalent to 60 tons of organic carbon and corresponded to 2.4 per cent of the weight of the cultivated layer. The actual increase of humus carbon compared with the control was 2.29 per cent. In this experiment, therefore, up to 95 per cent of the farmyard manure applied was fixed in the form of humus.

In addition, there are works showing that farmyard manure is a very limited source of humus. On the basis of an 11-year experiment in which farmyard manure was applied systematically to a light calcareous soil, Springer (1936) calculated that the content of organic carbon in the manured plot was higher by 0.25 per cent of the soil weight than in the control plot. In relation to the total amount of farmyard manure applied this increase was extremely small. The annual application of 4 tons farmyard manure (calculated as carbon) over 11 years provided 44 tons; in relation to the soil weight this amount of carbon of organic matter was 1.6 per cent. Thus, an increase in carbon of 0.25 per cent represented only 16 per cent of the total amount of farmyard manure applied, 84 per cent being completely mineralized.

Springer (1949) repeated his investigations and concluded after 22 years of the experiment that the systematic application of farmyard manure somewhat increased the percentage of humus in the soil. Addition of silt to the soil promoted the fixation of humus.

Kick (1951) reached similar conclusions that the loss of the major part of farmyard manure was as much as 80 per cent during the process of complete mineralization; his observations were made on podzolic soils. Dobrzański (1958) reached similar conclusions for sandy, clayey podzolic soil and clayey brown soil.

An intensive mineralization of farmyard manure was also demonstrated by Gericke (1946): 50 per cent was mineralized during the first year, 25 per cent during the second and 20 per cent during the third. Over a 3-year period, 95 per cent of the total amount of applied farmyard manure was mineralized and only 5 per cent remained in the form of humus.

The data of several long-term, farmyard-manure experiments on various soils of the USSR were evaluated in our laboratory. The subjects of the investigation were:

Sod-podzolic soils

(a) *Dolgoprudnaya Experimental Station*. A 6-course rotation on medium loam soil. The experiment was laid down in 1931, the field having undergone four complete rotations. Over the whole experimental period 1680 quintals/ha farmyard manure were applied, which calculated as carbon of dry matter is 210 q/ha.¹

(b) *The Timiryazev Academy of Agriculture*. Light loam soil. Fallow since 1912. During the experimental period, 6280 q/ha farmyard manure or 785 q/ha carbon of dry matter were applied.

(c) *The Potato Institute (Moscow region)*. Light sandy-loam soils. The experiment was laid down in 1931. The rotation was: seradella for hay-potatoes-oats. During the experimental period, the field underwent 6 rotations during which time 1800 q/ha farmyard manure or 225 q/ha carbon of dry matter were applied.

Chernozem soils

(a) *Kuznetsk Experimental Station*. Experiment laid down in 1937. 6-course rotation on slightly solodized, heavy-loam chernozem. 1400 q/ha farmyard manure or 175 q/ha carbon of dry matter were applied.

(b) *Sumsk Experimental Station*. Slightly solodized chernozem. Experiment continued since 1935. Rotation: fallow-winter wheat-sugar beet-spring wheat. From 1939 onwards perennial grasses were introduced into the rotation. The field underwent 3 complete rotations; during this time 2000 q/ha farmyard manure or 250 q/ha carbon of dry matter were applied.

(c) *Sumsk Experimental Station*. The data are from the work of Skvortsov (1938). Continuous sugar beet since 1912. During the experimental period 5200 q/ha farmyard manure or 650 q/ha carbon of dry matter were applied.

Typical serozem

The Ak-Kavak Experimental Station. Medium-loam typical serozem. Continuous cotton since 1926. During the experimental period 3830 q/ha farmyard manure or 478 q/ha carbon of dry matter were applied.

¹ It was assumed that the content of dry matter of farmyard manure is 25% and that the carbon content of the dry matter is 50%.

TABLE 97. CHANGE IN CONTENT OF ORGANIC MATTER IN LONG-TERM EXPERIMENTS WITH APPLICATION OF FARMYARD MANURE*
(Pankova and Bel'chikova)

Soil	Carbon of farm- yard manure applied (q/ha)	Sampling depth (cm)	Organic carbon in soil (%)			Increase of organic carbon	
			control	manured	increase	in q/ha	as % of applied farmyard manure to a depth of
Sod-podzolic soils: Six-course rotation (Dolgoprudnaya Experimental Station)	210	$\left\{ \begin{array}{l} 0-20 \\ 20-40 \end{array} \right.$	0.86	1.02	0.16	40	
			0.76	0.86	0.10	30 <u>70</u>	19.0 33.3
			0.79	1.16	0.37	92.5	
Fallow (Timiryazev Academy of Agriculture)	785	$\left\{ \begin{array}{l} 0-20 \\ 20-40 \end{array} \right.$	0.40	0.55	0.15	45.0 <u>137.5</u>	12.0 17.5
			0.61	0.75	0.14	31.5	—
Crop rotation (The Potato Institute)	225	0-18					
Chernozem soils: Six-course rotation (Kuznetsk Experimental Station)	175	$\left\{ \begin{array}{l} 0-25 \\ 25-35 \end{array} \right.$	5.00	5.10	0.10	31.3	—
			4.90	4.90	none	none <u>31.3</u>	17.8 17.8

TABLE 97 (cont.)

Soil	Carbon of farm-yard manure applied (q/ha)	Sampling depth (cm)	Organic carbon in soil (%)			Increase of organic carbon	
			control	manured	increase	in q/ha	as % of applied farmyard manure to a depth of
							0-20 cm 0-40 cm
Continuous sugar beet (Sumsk Experimental Station) (Skvortsov, 1938)	650	0-20	2.55	3.14	0.59	147.5	22.7
	250	0-20	2.57	2.73	0.16	40.0	16.0
Typical serozem:							
Continuous cotton (Ak-Kavak Experimental Station)	478	0-20	0.60	0.94	0.34	85.0	
		20-40	0.55	0.73	0.18	54.0	17.7
						139.0	29.0

* In the calculations the following weights were used for the soil layers:

0-20 cm layer 2.5 million kg per ha
 0-25 cm layer 3.125 million kg per ha
 0-18 cm layer 2.250 million kg per ha
 20-40 cm layer 3.0 million kg per ha

In the experiment mentioned the humus content of the soil samples was determined and the increase in humus in weight units on manured plots was calculated for the cultivated and sub-cultivated layers for an area of 1 ha; the calculations were made in respect to organic carbon both for farmyard manure and soil humus.

From a comparison of the values for the increase of humus-carbon on manured plots with the amount of carbon of farmyard manure applied during the experimental period, the part of the farmyard manure remaining in the soil in the form of humus was calculated.

In making the calculations it was assumed that the organic matter in the manured and control plots was decomposing at the same rate and that in both cases the introduction of additional organic matter in the form of root residues of the plant cover was of the same value.

The results of the investigations are given in Table 97.

As can be seen from Table 97, in all cases where farmyard manure was applied systematically the soil became richer in humus. The greatest increase was observed in the 0–20 cm layer. In soils of the adequate moisture zone (sod-podzolic) and irrigated serozems an increase in humus was also recorded for the sub-cultivated horizon where the organic matter is evidently washed down from the upper layer. In soils with limited moisture (chernozems of the Kuznetsk Experimental Station) there was no recorded increase in humus in the 20–40 cm horizon.

From a comparison of the values characterizing the amount of carbon of farmyard manure and from the increase of humus carbon in the soil it follows that only about 1/5 of the farmyard manure is fixed in the form of humus. 80 per cent of the manure is completely mineralized and may be consumed by micro-organisms utilizing farmyard manure as a source of energy; this part of farmyard manure is a source of plant nutrients and a source of carbon dioxide of the soil air.

There were no essential differences in the values characterizing the amount of farmyard manure converted into humus substances in different soils. Apparently, in long-cultivated soils (as in our experiments) any possible differences in the character of the decomposition of farmyard manure depending on soil climatic conditions are nullified.

It was of interest to find out in which direction the composition of the humus changed in manured soils compared with control soils. In a number of soil samples the composition of humus was determined according to Tyurin's scheme (Table 98).

From Table 98 it can be seen that with the increase in the humus content of the manured plots there is a corresponding increase in the content of

TABLE 98. COMPOSITION OF SOIL HUMUS IN LONG-TERM EXPERIMENTS WITH FARMYARD MANURE APPLICATION (Analyses by Pankova and Bel'chikova)

Soil and utilization	Organic carbon in soil (%)	Humic acids	Fulvic acids	Humic acid/fulvic acid ratio
Sod-podzolic soil: Fallow (Timiryazev Academy of Agriculture)				
Control	0.79	0.16* 20.3	0.25* 31.6	0.64
Manured	1.16	0.28 24.3	0.32 27.6	0.88
Typical serozem: Continuous cotton (Ak-Kavak Experimental Station)				
Control	0.78	0.16 20.5	0.18 23.0	0.89
Manured	1.10	0.23 20.9	0.23 20.9	1.0

* The top line of figures indicates the carbon content of the humic and fulvic acids as a percentage of the soil weight; the lower line indicates their percentage content in the humus composition.

humic acids and fulvic acids. Moreover, it is characteristic that the content of humic acid increases absolutely and relatively but that with the absolute increase in the content of fulvic acids their relative amount in the composition of the humus decreases. Hence, in manured plots, the ratio of carbon of humic acids to carbon of fulvic acids increases in both podzolic and serozem soils.

We have studied new data which have recently become available from experiments at the Timiryazev Agricultural Academy (Balev, 1949; Egorov, 1949, 1961; Lykov, 1961), at the Dolgoprudnaya Experimental Station (Koshel'kov and Osipova, 1956) and at the Ak-Kavak Experimental Station (Mukhanova, 1949; Belousov, 1955). These results confirm our conclusions both about the rate of decomposition of farmyard manure and about the change in composition of soil humus when farmyard manure is regularly applied. Therefore the following conclusions may be formulated with great conviction.

CONCLUSIONS

Soils systematically supplied with farmyard manure are found to have a higher humus content than control soils; the greatest humus accumulation is observed in the 0–20 cm layer and a somewhat smaller accumulation in the 20–40 cm layer. A slight increase in humus may also occur in the deeper horizons.

It was found from a comparison of the amounts of farmyard manure applied with the increases of humus in the soil, that from 2/3 to 3/4 of the total amount of farmyard manure was mineralized completely – increasing the soil fertility by providing nutrients, serving as a source of CO₂ for plants and as an energy-providing material for micro-organisms. The increase of humus in the soil amounted to only 1/3 to 1/4 of the total amount of farmyard manure applied.

As a result of the systematic application of farmyard manure the composition of the humus changes. It is observed to have a somewhat higher content of humic acids, and the humic acid/fulvic acid ratio becomes wider.

Thus, in our opinion, systematic fertilizing with farmyard manure is one of the measures favouring soil improvement, i.e. the accumulation of nutrients, the increase in the amount of humus and the intensification of biological activity. An increase in the content of mobile forms of humic acids in the composition of humus suggests that they may have a direct effect on the plant by stimulating growth and development.

However, farmyard manure has a weak effect in restoring soil structure owing to the way in which it is distributed in the soil. This was pointed out by Williams and confirmed in a number of investigations dealing with the structure of various soils (Pavlov, 1929; Savvinov, 1935; and others).

THE ACCUMULATION OF ORGANIC MATTER UNDER
NATURAL FALLOW¹

When the soil is left to natural fallow, perennial grasses gradually replace the weeds which are the first plants to develop on the loosened soil. The development on natural fallow of perennial grasses with strongly developed root systems favours the accumulation in the soil of humus;

¹ *Translators' note:* The Russian term *estestvennaya zalezh*, here translated as “natural fallow”, is used for land that has not been cultivated for a number of years, so that natural vegetation has re-established itself.

this takes place even during the growth of the plants, due to the death of parts of the root systems. A change from the aerobic conditions which exist under annual crops to the partial anaerobism occurring under perennial grasses favours both the formation and retention of humus in the soil. As a result the soil is enriched in humus and the loss in fertility caused by a preceding period of cultivation of annual crops is restored.

Leaving the soil to natural fallow has little practical importance at the present day; the system is used only in sparsely populated steppe regions. An examination of data on this question would be of great interest, however, to give an idea of the effect of a change in the plant association on the accumulation of organic matter. Unfortunately, the scanty data available on this subject are mainly for the zone of variable (and for the most part) inadequate moisture.

Attention is drawn to the work of Ivanov (1938), who studied the restoration of soil fertility under natural fallow in chernozems of the Kuibyshev region. His data show that the accumulation of humus under natural fallow takes place extremely rapidly (Table 99).

TABLE 99. ACCUMULATION OF HUMUS IN CHERNOZEM UNDER NATURAL FALLOW (Ivanov, 1938)

	The V.I. Lenin State Grain Farm				Kinel'sk Exp. Sta.		
	virgin land	old arable land	4-yr natural fallow	10-yr natural fallow	old arable land	3-yr natural fallow	10-yr natural fallow
Humus (%)	4.33	4.00	4.89	4.75	5.68	6.25	6.24
Accumulation (compared with old arable land)	—	—	0.89	0.75	—	0.57	0.56
As % of control (old arable land)	—	100	122	119	—	110	110

Unfortunately, neither the initial humus content prior to fallowing nor a description of the change in plant cover on natural fallow appear in Ivanov's work. In the absence of these data doubts arise as to whether the high humus content of young fallows, exceeding even its amount in virgin land, is due to the introduction of the fallow or whether it is explained by the different initial state of the fields.

Orlovskii (1935) carried out more detailed observations on the fallowing of old cultivated chestnut soil at the Uralsk Experimental Station. He

observed a strong suppression of accumulation processes. In spite of the close proximity of a virgin area, colonization with sheep's fescue and feather grass (*Stipa*) on the natural fallow was slow; for a long time only spring ephemerals developed intensively. For this reason, the restoration of humus and nitrogen in the soil under natural fallow proceeded slowly (Table 100).

TABLE 100. ACCUMULATION OF HUMUS AND NITROGEN IN CHESTNUT SOILS UNDER NATURAL FALLOW (Orlovskii, 1935)

	Sheep's fescue-feather grass virgin land	Old arable land	Natural fallow 5 yrs
Humus	2.57%	2.37%	2.39%
Nitrogen	0.18%	0.16%	0.17%
Humus as % of control	100	92	93

Detailed investigations on the change of composition of the vegetation in natural fallow of various ages on chernozems and chestnut soils of the Kustanaisk province were carried out by Khvorov and Onokhova (1939). From these observations they established the following stages in the change of vegetation:

On chernozem soil

Weed stage	1-3 yrs
Couch-grass stage	3-6 yrs
Couch grass-other grasses stage	6-8 yrs
Sheep's fescue-other grasses stage	9 yrs and over
Sheep's fescue-feather grass-mixed grass steppe	

On chestnut soil

Weed stage	1-5 yrs
Sedge-turf stage	5-30 yrs

Feather grass-sheep's fescue-steppe (virgin land)

Thus, the re-establishment of virgin land was accomplished in a shorter period on chernozems than on chestnut soils. The authors found large amounts of plant residues, amounting to 5-8 tons/ha in natural fallow

soils and 9 tons/ha in virgin land; sources for humus formation were thus present in adequate amounts in natural fallow.

On the basis of their data Khvorov and Onokhova consider that the restoration of humus is rapid under natural fallow. In their opinion, a complete restoration of humus takes place in chestnut soil over a period of 6 years. The authors base their conclusion on a comparison of the amount of humus in natural fallow with the amount in virgin land. It would have been more correct, however, to compare it with the amount of humus in the old arable land prior to natural fallowing.

We used data on the extent of the humus losses over a 10-year period following the ploughing of virgin land (see Tables 87 and 88) in compiling Table 101. A comparison of these data with values obtained for the increase in humus during fallowing showed that the rate of this process was not very high. Actually, if the loss of humus during the 10-year period of ploughing was 7.4 per cent of the amount in the virgin land (Table 101),

TABLE 101. ACCUMULATION OF HUMUS IN CHESTNUT SOIL UNDER NATURAL FALLOW (Khvorov and Onokhova, 1939)

Age of natural fallow	Content of humus (%)		Humus of natural fallow as % of that of virgin land	
	natural fallow	virgin land	at beginning of fallowing	at time of humus determination
Natural fallow 2-3 yrs old (after 15 yrs of cropping)	4.75	5.50	—	85.2
Natural fallow 6 yrs old (after 10 yrs of cropping)	4.08	4.22	92.6	95.4
Natural fallow 15 yrs old (after 10 yrs of cropping)	4.14	4.22	92.6	99
Natural fallow 20 yrs old (after 7 yrs of cropping)	5.47	5.58	94.3	98

only 2.8 per cent of this was restored during six years of fallowing. Complete restoration of the humus only occurred after a period of 15-20 years.

It is seen from a comparison of data on the decomposition of humus after the ploughing of virgin land and fallows with data on the restoration of humus in the latter, that in zones with inadequate moisture the transformation processes of organic matter proceed at a reduced rate. This is mainly due to the unfavourable water regime during the summer period of high temperatures, which inhibits biological activity.

As will be seen later, this pattern is also apparent from an examination of data characterizing the transformation processes of organic matter in artificial fallows after the sowing of perennial grasses.

THE CHANGE OF SOIL ORGANIC MATTER IN ROTATIONS WITH PERENNIAL HERBAGE¹

A large number of papers dealing with the effect of perennial herbage on the soil and on crop yields have appeared. In recent years, these studies have developed considerably and a number of points concerning the accumulation of root residues and humus and the improvement of the physico-chemical and physical properties of the soil can now be regarded as fairly clear.

The accumulation of root residues under perennial herbage

It has been found that large amounts of root residues accumulate under perennial herbage; for the cultivated layer these amounts have been estimated at several tons/ha. Data on this subject for the main soil-climatic zones can be found in review papers by Kulzhinskiĭ (1939), Chizhevskiĭ (1938), Nad'yarnĭi (1939), Baĭko and Popazov (1942), Mosolov (1946), Chizhevskiĭ and Kosinskiĭ (1947), Chizhevskiĭ and Lapuzin (1949) and Ivanov (1950). Data for the separate soil groups can be found in the work of Tiunov (1940) and Vorob'ev (1946) for sod-podzolic soils; for chernozems in the work of Mordovskiĭ and Pal'mina (1938), Sidorov (1947) Suchalkina and Kotlyarov (1949) and Petrushenko (1949); for chestnut soils in the work of Khvorov and Onokhova (1939); and for irrigated serozems in the work of L. I. and L. L. Golodkovskiĭ (1937), Meerson (1939), Kononova and Lagunova (1940), Belyakova (1947) and Dorman *et al.* (1949).

The extent of the accumulation of root residues depends on the age and species of the grasses and on the level of agriculture: the better the growth of the grasses the more the root systems are developed. Therefore, measures for increasing the yields of perennial herbage promote the development of the root systems and so increase their role in the restoration of soil fertility.

* *Translators' note:* In literal translation, the Russian term *mnogoletnie travy* means "perennial grasses". However, in this section the term is applied to mixtures of grasses with leguminous plants, such as clover and lucerne, and also to pure stands. The term has therefore been translated as "perennial herbage".

In Table 102, data are presented on the root reserve under perennial herbage in different soils. It should be borne in mind, however, that these data only permit an estimate of the order of magnitude of the values to be made, as variations of the latter are determined not only by the actual amount but also by the method of root counting employed by the different

TABLE 102. THE RESERVE OF ROOTS AND ROOT RESIDUES IN THE CULTIVATED LAYER UNDER A GRASS MIXTURE AND UNDER INDIVIDUAL SPECIES

Soil	Author	Utilization	Age (year of utilization)	Reserve of roots (q/ha)
Sod-podzolic soil	Vorob'ev, 1946	Clover and timothy	2nd	39.2
Forest steppe, chernozem	Kulzhinskiĭ, 1939	Clover and <i>Agropyron cristatum</i>	2nd	49.3
		Clover	2nd	38.8
	Nad'yarnyi, 1939	Lucerne and <i>Agropyron cristatum</i>	3rd	111.7
		Lucerne	3rd	106.9
Ordinary chernozem	Suchalkina and Kotlyarov, 1949	<i>Agropyron tenerum</i> + lucerne + <i>Agropyron cristatum</i>	2nd	73.2
	Bel'chikova, 1949	Lucerne and <i>Agropyron cristatum</i>	2nd	129.8
Southern chernozem	Petrushenko, 1949	Lucerne and <i>Agropyron cristatum</i>	2nd	53.5
	Kulzhinskiĭ, 1939	Lucerne and <i>Agropyron cristatum</i>	2nd	98.5
		Lucerne	2nd	46.6
Dark chestnut soil	Khvorov and Onokhova, 1939	Virgin land	2nd	38.5
		<i>Agropyron tenerum</i>	6 years	33.9
Typical serozem	Dorman, 1949	Lucerne	2nd	89-103
Light serozem	Kononova and Lagunova, 1940	Lucerne	2nd	66.7
Irrigated serozem	Belyakova, 1947	Lucerne	2nd	170-180
		Lucerne and grass	2nd	170-180

workers (the method of separating the roots from the soil, the size of the sieve through which washing of the roots is carried out, etc.).

The extent of the accumulation of roots and root residues under perennial herbage under a high level of agriculture can be judged from our data obtained at the Institute of Agriculture, Kamennaya Steppe. Here, the amount of roots and root residues under a grass mixture of the second year of utilization has been estimated, for the 0–40 cm layer, as 14.5 tons/ha, which approaches the value of the root reserve of uncut and cut steppe. For comparison, data are included on the amount of roots and root residues under the continuous cultivation of cereals and root crops in fields adjoining the collective farm “Vysokii”: here, the total amount of root residues in the 0–47 cm layer is only 5.8 tons/ha (Table 103).

It would be incorrect to assume that the amount of newly formed humus substances is determined merely by the amount of roots present in the soil at any given stage of plant growth; it should be borne in mind

TABLE 103. RESERVE OF ROOTS AND ROOT RESIDUES IN VIRGIN STEPPE UNDER GRASS–LUCERNE MIXTURE AND UNDER CEREALS (KAMENNAYA STEPPE) (Bel'chikova, 1949)

Utilization and depth of layer (cm)	Reserve of roots and root residues (q/ha)
Uncut steppe:	
0–8	121.2
8–24	40.2
24–41	21.3
Total:	182.7
Cut steppe:	
0–6	157.7
6–20	33.6
20–42	19.4
Total:	210.7
Lucerne and <i>Agropyron cristatum</i> of 2nd yr of utilization:	
0–20	129.8
20–40	14.7
Total:	144.5
Continuous cultivation of cereals and root crops (in 1949, oats):	
0–22	44.0
22–37	10.0
37–47	4.2
Total:	58.2

that during plant growth the root system is undergoing continuous regeneration.

In actual fact, during the estimation of root reserves, a certain number of rootlets at various stages of humification are always found, in addition to living roots (Table 104).

TABLE 104. CHARACTERISTICS OF ROOTS WITH DIFFERENT LAND UTILIZATION IN THE KAMENNAYA STEPPE (Bel'chikova)

Utilization and depth of layer (cm)	Volume of roots (cm ³ /l)				Weight of roots (q/ha)			
	living >2mm	living <2mm	dead	total	living >2mm	living <2mm	dead	total
Uncut steppe:								
0-8	4.0	20.0	36.0	60.0	13.8	37.6	69.8	121.2
8-24	2.0	6.0	4.2	12.2	11.6	16.6	12.0	40.2
Cut steppe:								
0-6	5.4	59.5	40.5	105.4	9.9	56.3	91.5	157.7
6-20	0.3	6.9	5.5	12.7	1.3	17.4	14.9	33.6
Lucerne and <i>Agropyron cristatum</i> of 2nd yr of utilization:								
0-20	5.6	7.6	10.4	23.6	45.9	29.4	54.4	129.7
20-30	0.5	3.2	1.3	5.0	3.5	4.5	1.8	9.8
Continuous cultivation of cereals and root crops:								
0-22	—	1.5	4.7	6.2	0.6	4.2	39.2	44.0
22-37	0.9	0.9	1.9	3.7	3.2	2.2	4.6	10.0

The extent of the regeneration of perennial-herbage roots is closely related to the condition of the plants. The longer the period of growth and the better the development of the plants, the greater is their role in humus formation and in increasing soil fertility. It is not surprising, therefore, that the highest values for the accumulation of roots and humus under perennial herbage are found under irrigated serozems: in this case, with good development of the grasses, the root reserve, even as early as the second year of growth, amounts to 12-15 tons/ha and the increase of humus in the cultivated layer to 0.4-0.5 per cent of the soil weight, or approximately 10-12 tons/ha.

We shall attempt to calculate the amount of root residues necessary for the formation of this amount of humus. As has already been pointed

out (see Chapter 3 and the review of the work of Hénin and Dupuis at the beginning of the present chapter), the humification coefficient of plant residues is approximately 0.4; the remaining 60 per cent of the components of plant residues is mineralized to final products during humification. Consequently, about 25–30 tons of root residues form 10–12 tons of humus; this value is 2–3 times greater than the amount of roots determined at any time during plant growth.

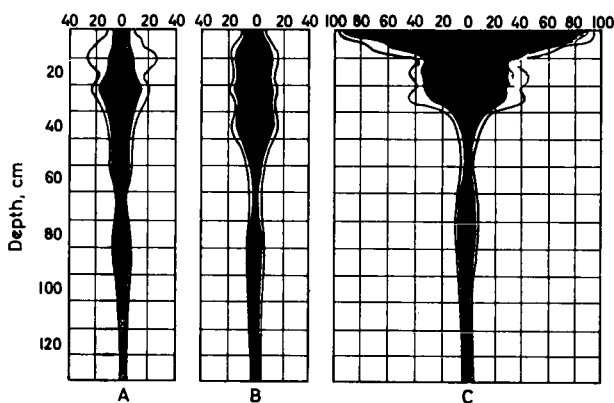


FIG. 73. The length of roots in mm per cc of soil (Savvinov — solonets of Malouzensk Station).

The black areas represent fresh, undecomposed roots; the light areas (together with the black area) represent the sum of fresh roots that have survived the winter and old half-rotted roots: (A) Irrigated wheat; (B) Irrigated *Medicago lupulina*; (C) Irrigated *Agropyron cristatum* (broad-eared).

This example confirms the opinion already expressed of the inaccuracy of calculations of the possible accumulation of humus under perennial herbage based on a single determination of the reserve of roots without taking into account their dynamics during the growth of the plant. An error of this kind was made by Hénin and Dupuis, who clearly underestimated the role of perennial herbage in the total balance of humus.

The characteristic feature of the root systems of perennial herbage is not only their total amount but also their length. A considerable amount of work in this connexion was done by Savvinov, who presented an original method of root counting (Savvinov and Pankova, 1942).

The available data indicate that the values for the length and volume of roots of perennial herbage in the soil are many times greater than the corresponding values for annual crops (Fig. 73).

Chizhevskii and Kosinskiĭ (1947) give the following figures for the total length of roots of lucerne and grass-lucerne mixture:

Roots of lucerne in an area of 1 sq m	744.8 m
Roots of lucerne in an area of 1 ha	7448 km
Roots of lucerne and ryegrass in an area of 1 sq m	2412 m
Roots of lucerne and ryegrass in an area of 1 ha	24,120 km

The total length of roots intermingling in the soil is thus 3 times greater with lucerne-ryegrass mixture than with lucerne alone; therefore, the roots of the mixture have a greater effect on the soil than the roots of the leguminous component by itself.

It is a well-known fact that the root systems of perennial herbage play a very great part in producing soil of good structure; this is the result of their physical action (pressure) and the subsequent impregnation of the formed aggregates with humus substances produced during the decomposition of rootlets.

An examination of the nature of soil structure and its manifold importance in the water-air and nutrient regimes of the soil will not be made here. Instead, we shall limit ourselves to providing a few examples to illustrate the role of perennial herbage in the formation of soil structure.

The role of perennial herbage in the formation of soil structure

Data on the effect of perennial herbage on soil structure can be found in most of the previously mentioned works in which the root mass under perennial herbage is calculated (see the previous section).

Similar data are given in the work of Savvinov (1935, 1936), Rostovtseva and Avaeva (1935), Taruntaeva (1942), Stolyarova (1947) for sod-podzolic soils; Red'kin (1941) for secondarily podzolized soils; Karabit-skaya (1932), Ivanov (1938), Sakharov (1938), Perederii (1941), Baïko and Popazov (1942), Tsÿganov (1948) for chernozems of various origin; Vorob'eva (1939), Khvorov and Onokhova (1939) for chestnut soils; Pavlov (1929), Gel'tser (1934, 1936), Ioffe (1930), Zhorikov (1930), Belyakova (1947), and others for irrigated serozems.

In Table 105, data for sod-podzolic soils of the Timiryazev Agricultural Academy (Taruntaeva, 1942) are given.

According to Taruntaeva, perennial herbage of the second year of

TABLE 105. AMOUNT OF WATER-STABLE AGGREGATES IN OLD CULTIVATED LAND AND UNDER HERBAGE ON SOD-PODZOLIC SOIL (Taruntaeva, 1942)

Subjects of investigation and depth of layer (cm)	Year of utilization	% water-stable aggregates > 0.25 mm
Old cultivated land:		
0-10	—	41.4
10-20	—	44.8
20-30	—	58.6
Clover:		
0-10	2nd	72.4
10-20	2nd	66.4
20-30	2nd	44.0
Timothy:		
0-10	2nd	71.8
10-20	2nd	66.4
20-30	2nd	63.0
Clover and timothy:		
0-10	2nd	79.4
10-20	2nd	73.8
20-30	2nd	70.0

growth (clover, timothy and clover-timothy mixture) has a considerable structure-forming effect on the soil.

The 2-3 mm aggregates isolated by Taruntaeva from under perennial herbage were found to be very water-stable, whereas aggregates of the same size from old cultivated land were rapidly destroyed by water.

TABLE 106. AMOUNT OF WATER-STABLE AGGREGATES IN CULTIVATED LAYER OF OLD CULTIVATED LAND AND UNDER HERBAGE IN ORDINARY CHERNOZEM (Baiko and Popazov, 1942)

Subjects of investigation	Year of utilization	% water-stable aggregates		
		> 1 mm	1-0.25 mm	<0.25 mm
Old cultivated land	—	23.6	44.5	31.9
Clover and timothy	2nd	51.9	33.2	14.9
Old cultivated land	—	22.3	21.1	32.0
Lucerne and timothy	2nd	53.0	32.6	14.4
Lucerne	2nd	40.6	32.8	26.6

Baiko and Popazov (1942) found that on ordinary chernozem of the Altai State Farm perennial herbage had a positive effect on soil structure (Table 106).

In Table 107, data are presented illustrating the structure-forming effect of perennial herbage on irrigated serozems.

TABLE 107. PERCENTAGE OF WATER-STABLE AGGREGATES IN OLD CULTIVATED SOIL AND UNDER PERENNIAL HERBAGE IN SEROZEMS (Belyakova, 1947)

Subjects of investigation and depth of layer (cm)	% water-stable aggregates > 0.25 mm
8 yrs under cotton:	
0-15	10-16
Virgin land:	
0-15	41-54
15-30	36-45
Lucerne in 3rd yr of growth:	
0-15	33-44
Lucerne in 2nd yr of growth:	
0-15	22-24
Lucerne + grass in 2nd yr of growth:	
0-15	26-28

What is the criterion for judging the transformation of structureless soil into soil of good structure? Williams indicated that "the threshold of damage", i.e. the number of pulverized particles filling all the interspaces of the soil crumbs, varied from 23 to 35 per cent of the soil weight. At this value, the soil loses the features characteristic of soil of good structure. A further increase in the number of pulverized particles, e.g. up to 40, 50 or 60 per cent, is without any effect.

It is evident from an examination of the literature cited that perennial herbage, and particularly grass mixtures, are in most cases a very important factor in producing a water-stable soil structure. However, even with a vigorous development of perennial herbage, the improvement in soil structure often does not reach the level indicated by Williams in the preceding paragraph.

The method of regenerating soil structure by polymers was discussed in Chapter 4.

*The dynamics of humus substances in rotations with perennial
herbage in different soil-climatic zones*

The data at present available from research and experimental establishments permit estimates to be made of the extent and rate of humus and nitrogen accumulation under perennial herbage during their growth, and also of the character of the decomposition of organic matter after the ploughing-up of grass. At the same time, certain specific features of the transformation processes of organic matter under different soil-climatic conditions are revealed; this is important for understanding the role of herbage in increasing soil fertility and for the development of rational methods for the utilization of the grass sod.

We shall examine corresponding data for sod-podzolic soils, chernozems of regions of moderate and variable moisture, chestnut soils of arid regions and irrigated serozems.

Sod-podzolic soils. A number of investigators (Kulzhinskiĭ, 1939; Taruntaeva, 1942; Stolyarova, 1947; Naïdina, 1951; Chekalov, 1952; and others) reported an increase in the content of humus and nitrogen under perennial herbage, the increase of humus being up to 0.4 per cent of the soil weight.

Similar values were recorded by Pankova (1958) during studies of the dynamics of humus and nitrogen in rotations including various crops on sod-podzolic soil of light mechanical composition ("Kolos" Collective Farm, Moscow region). The mass of roots under perennial herbage was as much as 15 tons/ha.

It can be seen from the data of Table 108, that under grasses of the second year of utilization the accumulation of humus compared with that under the last course of the rotation (bare fallow) is 0.5 per cent, which calculated for an area of 1 ha, is equal to 12 tons.

TABLE 108. HUMUS AND NITROGEN CONTENTS IN ROTATION FIELDS OF THE
"KOLOS" COLLECTIVE FARM

	Grass mixture of 2nd yr of utilization	Spring cereals after ploughing the grass	Potatoes in 2nd yr after grass	Bare fallow
% Humus	1.86	1.76	1.38	1.36
% Nitrogen	0.125	0.112	0.097	0.098
Humus (kg/sq m)	5.37	4.78	3.51	3.33

However, as can be seen from Table 108 and Fig. 74, a rapid decomposition of humus takes place after the ploughing-up of the grass with the result that even after 2–3 years its content returns to the original value.

Similar results were also obtained during studies of the hydrophysical properties of these soils. Gussak, Dimo and Pankova (1950) reported that under perennial herbage the permeability, structure and resistance to erosion of the soil considerably improved. However, after ploughing-up

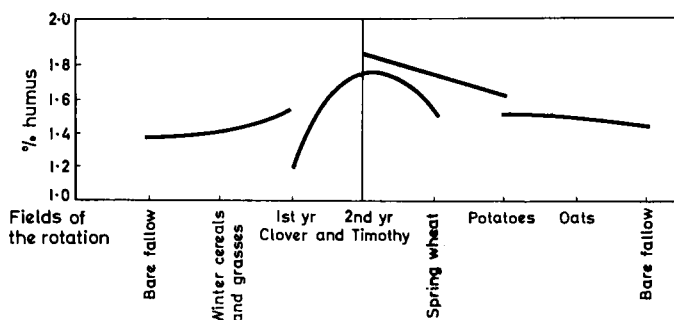


FIG. 74. The dynamics of the humus content (0–2-cm layer) in a rotation. Each curve is for a specific field of the rotation. Sod-podzolic soil (Moscow region), 1949–1951. (Data of N. A. Pankova).

the grass, the hydrophysical properties of the soil rapidly deteriorated. On heavy sod-podzolic soils grasses showed a more prolonged positive effect.

Vorob'ev (1946, 1947, 1950), Naïdina (1951), Baranovskaya (1952), and others also give an indication of the intensive humus formation under perennial herbage in various sod-podzolic soils (0.3–0.4 per cent of the soil weight or 7.5–10 tons/ha) and of the rapid decomposition of humus after the ploughing-up of the grass sod, particularly in the southern part of the zone of sod-podzolic soils.

The high intensity of the transformation processes of organic matter in rotations which include perennial herbage under the conditions of sod-podzolic soils of the southern part of the zone is explained by the fairly active microbial activity (see Chapter 5). The mineralogical composition (in particular, the low content of the colloidal fraction) of podzolic soils does not favour the fixation of humus substances and therefore is one of the causes of the low stability of the humus.

Thus, perennial herbage (providing its growth is good) plays a considerable role in restoring the fertility of sod-podzolic soils. However, on these soils the effect of the grasses is limited to 2–3 years.

Chernozems of regions of variable moisture. Many authors showed in their investigations that in chernozems of variable moisture, as in sod-podzolic soils of the southern part of the zone, perennial herbage under good management gives high yields and enriches the soil in organic matter in the form of root masses, humus and nitrogen. Thus, according to Petrushenko (1949), Tsýganov (1948), Suchalkina (1949, 1950, 1953), Kononova and Bel'chikova (1953), and other authors, the root masses of grass mixtures amount to 10–15 tons/ha and the increase in humus to 0.3–0.4 per cent of the soil weight.

Moreover, in a study of the dynamics of humus and nitrogen in a rotation, a high stability of the humus was observed in these soils compared with sod-podzolic soils. An example of this is provided by the data of Suchalkina (1950, 1953), who investigated the dynamics of humus and nitrogen in ordinary chernozem of the Kamennaya Steppe (Institute of Agriculture) in two rotations: between forest belts and in open steppe (Table 109 and Fig. 75).

TABLE 109. CONTENTS OF HUMUS AND NITROGEN IN FIELDS OF A ROTATION (Suchalkina, 1953)

	Winter wheat 1944	Grass and lucerne 1945	Spring wheat 1946	Spring wheat 1947	Sun- flower 1948	Oats 1949	Bare fallow 1950
% Humus:							
between forest belts	8.40	8.71	8.81	8.77	8.71	8.58	8.51
in open steppe	8.31	8.53	8.62	8.58	8.53	8.46	8.43
% Nitrogen:							
between forest belts	—	0.471	0.489	0.476	—	0.432	—
in open steppe	—	0.431	0.472	0.467	—	0.417	—

Here in contrast to sod-podzolic soils, some accumulation of humus is observed not only under grass but also under a crop of spring wheat following grass; this can be attributed to the predominance of the new formation of humus substances over their decomposition during the humification of the sod. A decrease in the humus content is only observed in the second or third year but at the end of the rotation cycle the soil is found to have a somewhat higher humus content than at the beginning. Consequently, one can expect a gradual increase in the humus content and, at the same time, an increase in soil fertility with each successive cycle of the rotation.

The cause of the relatively high stability of humus in chernozems is, firstly, the more moderate character of the microbial activity (see Chapter 5) limited here by the variable moisture regime during the summer period of high temperatures and, secondly, by the mineralogical composition of chernozems, particularly the high content of the colloidal fraction, permitting the fixation of humus substances by the mineral part of the soil. Here, the soil structure is also relatively stable.

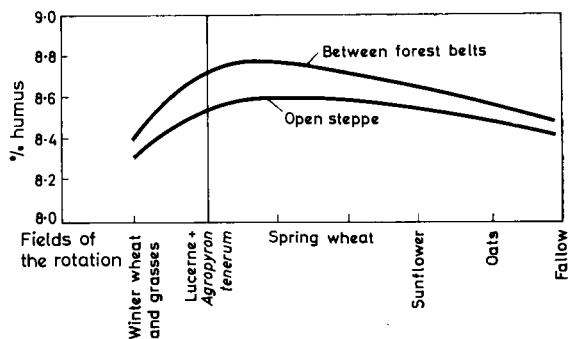


FIG. 75. The dynamics of the humus content (0–20 cm layer) in rotation. Ordinary chernozem (The V. V. Dokuchaev Institute of Agriculture, 1944–1950). (Data of M. I. Suchalkina).

Consequently, in chernozem soils of variable moisture under good growth of herbage, a more prolonged residual effect on the following crops can be expected than in sod-podzolic soils.

Chernozem and chestnut soils of arid regions. Numerous investigators have noted the small effect of perennial herbage in restoring soil fertility in arid regions of the European part of the USSR and in Kazakhstan (Savvinov, 1936; Chizhevskii, 1938, 1940; Kulzhinskiĭ, 1939; Livanov, 1947; and Rubinstein, 1956). The poor development of grass under these conditions is attributed to the moisture deficiency and also to the limiting effect of this deficiency on the activity of micro-organisms. Accordingly, the processes of new formation of humus substances proceed feebly under these conditions.

According to the data of Khvorov and Onokhova (1939), Kulzhinskiĭ (1939), Ivanov (1950), Vorob'eva (1939), Rubinshtein (1956), the accumulation of humus under grass under the conditions of these zones amounts to only 0.1–0.3 per cent. A feebly expressed accumulation of humus was also observed in chestnut soils by Orlovskii (1935), Lopato and Sidorov (1941).

During a study of the organic matter of chestnut soils and residual solonchak-like columnar solonets over several years, we could find (1943) no noticeable changes in the percentages of humus and nitrogen under grass and after ploughing-up the sod. Our conclusions were confirmed by Filippova (Antipov-Karataev, Pak and Filippova, 1950, 1955) and also by Glotova (1956).

Our observations (1943), like those of other investigators (Dukhanin, 1940; Livanov, 1947; Avdonin, 1946) revealed only slight decomposition of the root residues of perennial herbage over a long period.

From what has been said, it can be concluded that under the conditions of chernozem and chestnut soils of arid regions perennial herbage has only a weak effect on the restoration of soil fertility.

With regard to the organic-matter regime, irrigated serozems are in complete contrast to these soils.

Irrigated serozems. There have been detailed investigations on the problem of the accumulation of humus under perennial herbage in irrigated serozems. Relevant data for Central Asia are given in the works of Ioffe (1930), Gel'tser and Lasukova (1934), Golodkovskii, L. I. and Golodkovskii, L. L. (1937), Dorman (1938), Ryzhov and Tsybul'skaya (1938), Meerson (1938), Bolotnikova (1938), Sinyagin (1939), Kononova and Lagunova (1940), Bel'yakova (1957), Ryzhov and Dorman (1956), Malinkin (1957). Data for irrigated serozems of Azerbaidzhan can be found in the work of Dolgov *et al.* (1954), Aliev (1961) and Edigarova (1961).

According to the data of these authors the increase of humus under perennial herbage (relative to pure stands of lucerne) is 0.4–0.5 per cent of the soil weight, which for the cultivated layer amounts to 10–12 tons/ha. Taking into consideration the low humus content of serozems these increases represent 20–50 per cent of the total humus content. Therefore, the replenishment of humus in irrigated serozems under perennial herbage takes place on an enormous scale.

Extremely important is the fact that under the conditions of irrigated serozems with a high standard of grass management, the restoration of fertility (including the replenishment of humus) takes place rapidly during the first two years of growth (and utilization) of the herbage. In the third year, the accumulation of humus continues, but already at a somewhat reduced rate (Bolotnikova, 1938; Dorman, 1949; Ryzhov and Tsybul'skaya, 1938; Balyabo, 1949).

The supplementation of the reserve of easily mobilized forms of organic nitrogen proceeds with great intensity in irrigated serozems. Thus, according to our data, the nitrifying capacity of soils at the expense of soil

nitrogen under lucerne was highest under a 2-year-old stand; under 3-year-old lucerne the soil showed no greater nitrifying capacity than it did under 2-year-old lucerne (first part of Table 110).

Very important also, and characteristic for irrigated serozems, is the rapid decomposition of humus substances and the intensive mineralization of nitrogen-containing organic compounds after the ploughing-up of perennial herbage. We observed the clear dynamics of the process of accumulation-decomposition of humus in a rotation on serozems (Fig. 76).

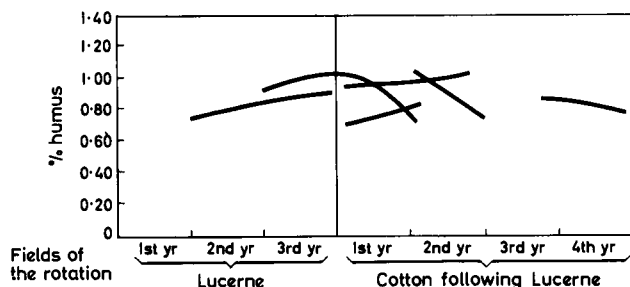


FIG. 76. The dynamics of the humus content (0–20 cm layer) of soils in a cotton–lucerne rotation. Each curve corresponds to specific points in the rotation fields. Light serozem. (Kazakhsk SSR). (Data of M. M. Kononova and E. P. Lagunova).

The observations were made on the same fields during the course of 3 years (1937–39). Following the ploughing of the lucerne field the lucerne roots rapidly decomposed under cotton; this is evident from our data (1940).

As can be seen from these data, 40 per cent of the total reserve of lucerne roots decomposed during the first year following the ploughing of the lucerne field for cotton. During the second year decomposition continued, but not so rapidly as in the first year (20 per cent); afterwards, it appears that difficultly and slowly decomposable components of the lucerne roots remain, since the amount of the latter showed practically no further change.

Stand	Amount of roots	
	(q/ha)	(%)
Lucerne of the 3rd yr of growth	103.3	100.0
Cotton of the 1st yr of growth following 3-yr-old lucerne	62.1	60.0
Cotton of the 2nd yr of growth	41.6	40.0

N.B. During the estimation of the plant residues the cotton roots were separated from the lucerne roots and taken into account.

The rate of decomposition of nitrogen-containing organic substances in the soil after the ploughing of the lucerne field is similar, as can be seen from the value of the nitrifying capacity at the expense of soil nitrogen (second part of Table 110); it is high under lucerne of the second year of growth but rapidly decreases under cotton during 2 years.

TABLE 110. NITRIFYING CAPACITY UNDER LUCERNE AND COTTON; $\text{NO}_3\text{-N}$ PER 100 g SOIL (Kononova and Lagunova, 1940)

Stand	Content of $\text{NO}_3\text{-N}$		
	initial	final	increase
Lucerne of 1st yr of growth	traces	10.9	10.9
Lucerne of 2nd yr of growth	18.3	39.9	21.6
Lucerne of 3rd yr of growth	traces	20.3	20.3
Ploughed lucerne			
Cotton of 1st yr of growth	none	15.0	15.0
Cotton of 2nd yr of growth	none	10.4	10.4
Cotton of 3rd yr of growth	none	8.7	8.7

Detailed investigations on the persistence of the residual effect of perennial herbage on the fertility of serozems were carried out by Belyakova (1947, 1957) and Antipov-Karataev (1950).

The amount of humus accumulated under perennial herbage is 0.4–0.5 per cent of the weight of the cultivated layer or 10–12 tons/ha. It has also been established that after ploughing a grass field for cotton a rapid decrease in the amount of humus occurs under the cotton crop. The residual effect of perennial herbage in irrigated serozems is limited to a period of not more than 4 years and by the fifth year the field shows little difference from old arable land (Table 111).

Similar examples are given in the works of Golodkovskii, L. I. and Golodkovskii, L. L. (1937), Meerson (1938), Dorman, Sokolov and Bodrov (1949), and other authors. Thus, Golodkovskii, L. I. and Golodkovskii, L. L. after calculating average productivity values for several experimental stations and subsidiary centres in Central Asia, found that during the first three years after the ploughing of a lucerne field the yield of raw cotton exceeded the yield on old cultivated land by 19–22 q/ha. However, this increase occurred mainly during the first two years of the residual effect of the lucerne: it amounted to 10–11 q/ha in the first year after lucerne, 7–8 q in the second year, and 2–3 q in the third. Similar data were obtained by Belousov (see Meerson, 1938): over three years the total increase in raw

TABLE 111. DURATION OF RESIDUAL EFFECT OF PERENNIAL HERBAGE ON COTTON YIELDS, HUMUS CONTENT AND AMOUNT OF AGGREGATES IN SOIL (Antipov-Karataev, 1950)

Subjects of investigation	Before ploughing	Years after ploughing					Cotton land 7-10 yrs after ploughing virgin land
		1st	2nd	3rd	4th	5th	
Three-yr-old lucerne—pure stand:							
Yield of raw cotton (q/ha)	—	49	46	40	38	28	26-30
% humus	1.90	1.85	1.75	1.50	1.45	1.40	1.2-1.3
Aggregates >0.25 mm	29	26	26	22	21	21	17-20
Three-year-old lucerne + cocksfoot + ryegrass:							
Yield of raw cotton (q/ha)	—	52	42	39	40	—	27-33
% humus	2.10	1.93	1.90	1.82	1.50	—	1.44-1.50
Aggregates >0.25 mm	31	29	29	23	24	—	—

cotton was 19 q/ha, the increase being 8.7 q in the first year after ploughing the grass field, 7 q in the second year and 3.3 q in the third.

Taking into consideration the rapid decomposition of organic matter in irrigated serozems after the ploughing of a grass field, the working-out of methods for the regulation of the decomposition processes of the grass sod is extremely important. Antipov-Karataev and Belyakova (1954) suggested that ploughing should be done to a depth of 35-45 cm without turning the furrow slice; in this case, the sod is placed at the bottom of the furrow and in the following years is gradually brought into the upper soil layers by ploughing.

As a result of the retardation of decomposition processes of the plant residues under these conditions, the effectiveness of the positive action of organic matter is prolonged.

CONCLUSIONS

Examination of the data shows that natural conditions for the development of perennial herbage for its action on the soil are most favourable in the irrigated serozems of Central Asia and Azerbaidzhan. Conditions are also reasonably favourable in the sod-podzolic soils of the southern part of the zone and in the chernozems of the central European belt of the USSR.

In chernozems and chestnut soils situated in arid regions (Trans-Volga region, Kazakhstan), unirrigated perennial herbage develops poorly, gives

low yields and does not contribute to the accumulation of humus or nitrogen in the soil. Under these conditions, agricultural practice has shown that the introduction of perennial herbage is uneconomic.

Without doubt, perennial herbage plays an important role in the accumulation of humus and nitrogen in irrigated serozems and sod-podzolic soils. It should be pointed out, however, that it is in precisely these soils, which are characterized by vigorous micro-organism activity and by limited fixation of humus (because of the low mineral colloid content of the soils), where there is a rapid decrease in humus and nitrogen after ploughing grassland. It is therefore important to develop methods of controlling the decomposition of organic matter (aiming at its longest possible utilization) after grassland has been ploughed.

INHIBITING EFFECT OF FRESH PLANT RESIDUES ON PLANT GROWTH

The deleterious effect of fresh or only partially humified plant residues on plant growth is fairly well known in agriculture; it is observed after the ploughing-in of cereal stubble and after the application of manure containing a large amount of undecomposed straw, and is usually attributed to the conversion of mineral nitrogen into nitrogen of the plasma of micro-organisms; the latter develop vigorously during the early stages of humification of plant residues.

A similar phenomenon is also observed during the cultivation of a crop on poorly decomposed sod of perennial herbage; this usually takes place with late dates of sod-ploughing, particularly under dry conditions.

However, even under irrigated conditions, a deleterious effect of poorly decomposed sod of perennial herbage was observed on cotton. Thus, in the works of the Ak-Kavak Experimental Station (Dorman, Sokolov, Bodrov, 1949) it was pointed out that the emergence of cotton plants grown on poorly decomposed lucerne sod was suppressed for a time. The death of some of the young plants was observed, particularly where the lucerne roots were poorly decomposed. Later, 2-3 weeks after the emergence of the seedlings, the plants assumed a normal appearance and outgrew the cotton plants in fields where lucerne was ploughed-in during earlier years; however, the stands still remained sparse.

The deleterious effect was also produced by a green-manure crop if ploughing was carried out immediately before the sowing of the following crop. Gel'tser (1936) pointed out that the growth of cotton sown immediately after ploughing-in a green manure was markedly depressed. This

was not observed, however, when a 10-day interval was allowed to occur between the time of ploughing of the green manure and the time of sowing of the cotton. According to Gel'tser the deleterious effect is caused by the high concentrations of NH_3 formed during the early stages of decomposition of the green manure.

As a result of numerous investigations, it can be assumed that the deleterious effect of fresh plant residues on the plant is determined by the interrelationship between the plant and the microflora participating in the decomposition of these residues, namely by their competition both for nutrients and for the oxygen of the soil.

Boussingault and Lewy (1852) and Fodor (1875) indicated that the decomposition of organic matter in the soil is accompanied by the formation of CO_2 , and because of the weak diffusion of the latter its content in the soil air increases and the O_2 content decreases (Table 112).

TABLE 112. CONTENTS OF CO_2 AND O_2 IN SOIL AIR UNDER DIFFERENT CONDITIONS OF CULTIVATION (Boussingault and Lewy, 1852)

Composition of air	Sandy soil, unmanured	Sandy soil	Black clayey soil	Fertile moist soil
Content as % of air volume:				
CO_2	1.06	9.74	0.66	1.79
O_2	19.72	10.35	19.99	19.41
Total:	20.78	20.09	20.65	21.20

The literature on the determination of CO_2 in the soil air (for summaries, see the works of Lundegårdh, 1927; Kononova, 1937; Gorbunov, 1941) provides evidence that the decomposition of plant residues, particularly at early stages, is accompanied by the formation of a large amount of CO_2 .

For this reason, we should expect to find a decrease in the amount of oxygen in the soil air during the early stages of humification. At the same time, the presence in decomposing plant residues of substances capable of processes of oxidation \rightleftharpoons reduction influences the oxidation-reduction condition of the whole system: soil-humifying plant residues.

It is clear, therefore, why numerous investigators observed a decrease in the oxidation-reduction potential when fresh organic matter was applied to the soil (Burrows and Cordon, 1936; Sturgis, 1936; Volk, 1939). We observed a similar phenomenon (1944) during the early stages of humification of lucerne roots.

Our experiments were carried out as follows: 400 g soil samples mixed with 20 g lucerne roots cut into portions 1–5 cm long were placed in 500 ml glass vessels provided with bottom drainage; the soil was slightly compressed and into it smooth platinum electrodes calibrated in buffer solutions were inserted. In each vessel, two electrodes were placed at the centre of the soil layer. An agar bridge was placed with one end in the soil and the other end in a beaker containing saturated KCl solution.

After installing the electrodes in the soil, the soil was brought to a moisture level corresponding to 60 per cent of the maximum water-holding capacity by introducing a calculated volume of water into a tube inserted in the drainage hole.

Later in the experiment, the moisture level was kept constant by adding water from above and below on the day before the measurement of the redox potential. The data obtained are in mV for a hydrogen electrode.

The first experiment was carried out with the cultivated layer of dark chestnut soil. The results of the Eh measurements are given in Table 113.

TABLE 113. Eh VALUE IN mV IN AN EXPERIMENT ON THE DECOMPOSITION OF LUCERNE ROOTS IN DARK CHESTNUT SOIL OF THE ERSHOVSK STATION

	Initial Eh value	Duration of experiment (days)						
		4	10	20	27	44	60	108
Dark chestnut soil:								
electrode No. 1	540	520	460	500	480	490	480	480
electrode No. 2	535	505	470	520	490	510	480	475
Dark chestnut soil + lucerne roots:								
electrode No. 1	540	70	140	420	430	410	500	450
electrode No. 2	530	105	130	380	440	420	505	460

It can be seen from the data of Table 113 that in the vessel containing roots the oxidation–reduction potential dropped markedly at the beginning of the experiment, then rose, and 20 days after the start of the experiment it approached that of the control. However, complete equalization of the Eh in the control vessel with that in the vessel containing roots did not occur until approximately 2 months from the start of the experiment.

For the second experiment (carried out by Lagunova) a syrt clay of the Ershovsk Station (Saratov region) was taken from a depth of 90–100 cm. The arrangement of the experiment was the same as before; its duration

was 2 months. The results of the determination of oxidation-reduction potential are given in Table 114.

In this experiment the trend of changes in the oxidation-reduction potential was the same as in the first experiment. With the introduction of roots into the soil the Eh dropped sharply at the beginning, then rose gradually, until near the end of the experiment no difference was apparent between the control vessel and the vessel with the roots. In this experiment rH values were calculated from the formula:

$$rH = \frac{Eh}{0.029} + 2pH$$

The results of the calculations are presented in Table 115.

The data on rH given in Table 115 show that during the early stages of decomposition of lucerne roots partially anaerobic conditions were produced in the soil, evidence of this being the low rH value (17.2). Later, the rH value gradually rose to 22.02, and after 18 days to 24.94, indicating the onset of aerobic conditions. However, complete equalization with the control only occurred $1\frac{1}{2}$ –2 months after the start of the experiment.

The oxygen deficit observed in the soil air during the first stages of humification of lucerne roots must have some effect on the plant. There are indications in the literature that most plants grow poorly with a decreased oxygen content of the soil medium because of the development of reducing processes and the decreased rate of root respiration (Kudryavtseva, 1924; Lundegårdh, 1931; Chernenkov, 1936; and others). Filippenko (1940) showed that the partial anaerobic conditions under which wheat vernalization is carried out considerably suppress the growth and development of the plant and favour the accumulation of a large amount of alcohol in the seeds.

To test the validity of the hypothesis that plants and microflora compete for nutrients and oxygen in the medium during the early stages of humification of plant residues, Bel'chikova, in our laboratory, carried out a number of experiments.

Experiment 1. This experiment, like the following experiments, was carried out in 500 ml glass pots. 400 g samples of clay soils from the Moscow area and 16 g samples of cut lucerne roots were used. To neutralize the acidity, each vessel received 1.6 g of CaO, which brought the pH of the medium to 7.6. The duration of preliminary humification of the roots was 3, 75 or 180 days. The test plant was barley.

In each pot 10 barley seeds were sown. After emergence and thinning, 5 plants were left in each pot. The plants were harvested at the shooting

stage (40 days after sowing). The results of the experiments are presented in Table 116.

TABLE 116. DEVELOPMENT OF BARLEY IN EXPERIMENT 1 WITH CLAY SOIL

Treatment	% emergence at surface	Time (days) from sowing to:			
		full emergence	2nd leaf	3rd leaf	shooting
Duration of humification of lucerne roots before sowing barley:					
3 days	100	9	11	20	24-30
75 days	100	5	5	11	15
180 days	100	5	5	11	15

The data given in Table 116 show the inhibition of emergence and further development of barley grown in pots containing undecomposed lucerne roots.

In these pots the plants showed signs of suppressed growth, the leaves being yellowish in colour right from the beginning of the experiment. Later, these symptoms were less evident but had not disappeared completely even at the end of the experiment. In pots containing roots decomposed for

TABLE 117. AIR-DRY WEIGHT OF AERIAL PARTS AND TOTAL NITROGEN CONTENT OF BARLEY

Treatment	Total weight of five plants (g)	Average weight of plants (g)	Total N content (mg)	
			of 5 plants	of 1 plant
Period of humification of lucerne roots before sowing barley:				
3 days				
I	0.77	0.16	21.8	4.4
II	1.08	0.22	25.8	5.2
75 days				
I	2.84	0.57	52.6	10.5
II	2.70	0.54	56.1	11.2
180 days				
I	3.24	0.65	87.1	17.4
II	3.16	0.63	91.1	18.2

a longer period, the plants showed normal development and there were no differences between the second and third treatment.

At the end of the experiment the plants were removed from the pots and the root systems were washed and photographed (Fig. 77). The plants were then air-dried, weighed and their total nitrogen content was determined by the Kjeldahl method (Table 117).



FIG. 77. The development of barley in pots (5 plants per pot) with soil and lucerne roots.

1. Lucerne roots decomposed for 3 days; 2. The same for 75 days; 3. The same for 180 days.

It can be seen from Experiment 1 that the poorest development, lowest weight and lowest amount of nitrogen were found in plants grown in pots containing undecomposed roots.

It might be thought that one of the causes of the poor development in this experiment was a deficiency of phosphorus and nitrogen in the clay and that the application, therefore, of a suitable amount of these elements would eliminate the deleterious effect of the plant residues during their early stages of decomposition. However, further experiments showed that the application of mineral fertilizers to pots containing undecomposed lucerne roots only partially removed the deleterious effect. Moreover, the simultaneous application of undecomposed lucerne roots and mineral fertilizers decreased the effectiveness of the latter.

Experiment 2. In this experiment, dark chestnut soil (cultivated horizon) from the Ershovsk Station was taken. The layout of the experiment was similar to that of Experiment 1. In some of the pots $(\text{NH}_4)_2\text{SO}_4$ and superphosphate were applied at rates of 0.1 g N and 0.1 g P_2O_5 per pot. The plants were harvested at the tillering stage 24 days after sowing. The results of the experiment are given in Table 118.

TABLE 118. DEVELOPMENT OF BARLEY IN EXPERIMENT 2 WITH DARK CHESTNUT SOIL

Treatment	% emergence at surface	Number of days from sowing to:			
		full emergence	2nd leaf	3rd leaf	tillering
Undecomposed lucerne roots	80	none	12	15	23-25
Without roots, with NP	100	6	6	12	17
Undecomposed lucerne roots + NP	90	none	8	13	19-20

The appearance of the plants was best in the second treatment (soil + NP) and poorest in the first treatment (soil + undecomposed lucerne roots). Where mineral fertilizers were applied to pots containing undecomposed lucerne roots the plants were of poorer development than those in pots receiving mineral fertilizers only. It was evident from the total weight of the plants and their nitrogen content (Table 119) that differences in their development persisted right up to the end of the experiment.

Thus, the cause of the deleterious effect on the plant of undecomposed and poorly decomposed plant residues is considerably more complicated. It is not entirely due to nutrient deficiency, as supplementary fertilizing only partially eliminated the effect. Moreover, the deleterious effect of

TABLE 119. WEIGHT OF AIR-DRY AERIAL PARTS AND TOTAL NITROGEN CONTENT OF BARLEY. EXPERIMENT 2

Treatment	Total weight of 5 plants (g)	Average weight of plant (g)	Total N content (mg)	
			of 5 plants	of 1 plant
Undecomposed lucerne roots:				
I	0.37	0.07	16.6	3.3
II	0.29	0.06	14.9	3.0
Without roots, with NP:				
I	1.36	0.27	65.7	13.1
II	1.68	0.34	82.5	16.5
Undecomposed lucerne roots + NP:				
I	1.09	0.22	52.0	10.4
II	1.29	0.26	61.8	12.4

undecomposed lucerne roots on barley began to show even at the time of emergence, i.e. before the plant required nutrients from the soil.

Experiment 3 was carried out with the cultivated horizon of dark chestnut soil. The size of the pots and the amounts of soil and lucerne roots were the same as in the two previous experiments. The duration of preliminary humification of the lucerne roots was as follows: (1) a long period of decomposition (5 months); (2) a short period of decomposition (17 days); (3) undecomposed roots.

In addition, control pots and pots with mineral fertilizers (N or NP) were included. All treatments except the control were brought to the same nitrogen level, for which purpose the original amount of NO_3 in the soil and composts was preliminarily determined. The highest NO_3 content (52 mg $\text{NO}_3\text{-N}$ per pot) was found in pots where lucerne roots were humified for 5 months; in the remaining treatments N was added in the form of NaNO_3 up to this level. In some of the pots $\text{Ca}(\text{H}_2\text{PO}_4)_2$ was applied at the rate of 52 mg P_2O_5 per pot. The fertilizers were applied at sowing as dilute solutions, partly at the surface and partly down a tube. The plants were harvested at the shooting stage. Data on the development of the plants are presented in Table 120.

The strongest and most rapid development of barley was observed in the treatment in which lucerne roots were subjected to a long period of decomposition. Evidently, in this case, the plant was adequately provided with nitrogen and phosphorus as the development of the plant and the

TABLE 120. DEVELOPMENT AND WEIGHT OF AERIAL PARTS OF BARLEY IN EXPERIMENT 3 WITH DARK CHESTNUT SOIL

Treatment	% emergence at the surface	Number of days from sowing to:					Weight of air-dry aerial parts (g)	
		full emergence	2nd leaf	3rd leaf	tillering	shooting	of 5 plants	of 1 plant
Long period of decomposition (5 months) of lucerne roots	100	6-9	8	12	15	20	I* 2.76 II 1.94	0.55 0.39
As above + P	80	none	8-9	12	15-16	20	I 2.58 II 1.82	0.52 0.36
Short period of decomposition (17 days) of lucerne roots + N	100	5	8	12-13	16-19	21	I 1.49	0.30
Undecomposed lucerne roots + N	100	5	10	15-16	—	34	I 0.17 II 0.16	0.03 0.03
N + P	100	5	8	12	15	20	I 2.30 II 2.11	0.46 0.42
N	100	5	8	12	15-19	24	I 1.03 II 1.04	0.21 0.21
Control	100	5	8	14	—	—	I 0.33 II 0.38	0.07 0.07

* Replicates.

yield were similar to that of N+P treatment. An additional phosphorus application to pots containing lucerne roots decomposed for a long period did not increase the yield.

As in the first two experiments, the poorest plant development was observed where the treatment with lucerne roots was given shortly before sowing; in this case the yield amounted to 15 per cent of that of the control (soil+N) and only 7 per cent of the yield from the treatment with a long period of root decomposition, regardless of the fact that the N levels were equal in all the treatments.

Data for the development and yield of barley in the treatment with a short period of decomposition (17 days)+N were similar to those obtained with a long period of humification of lucerne roots.

Experiment 4. This experiment was carried out with the cultivated horizon of light serozem. The size of pots and amounts of soil and lucerne roots were the same as in the previous experiments. The individual treatments at sowing were brought to the same nitrogen level as the treatment with a long period (5 months) of root decomposition, i.e. 55.3 mg $\text{NO}_3\text{-N}$ per pot.

Data on the development of barley and the air-dry weight of the aerial parts are given in Table 121.

The results of Experiment 4 with light serozem are similar to those obtained in the first three experiments: the best plant development and the highest yield were obtained in the treatments in which lucerne roots had been decomposed for a long period and the poorest development was observed with undecomposed roots. As in the previous experiments the inhibiting effect of the fresh roots began to show even at the time of emergence.

The yield in the treatments with undecomposed roots amounted to approximately 3 per cent of the yield with a long period of decomposition and 10 per cent of that of the treatment "soil+N", regardless of the fact that initially all the treatments were brought to the same nitrogen level.

The results of Experiments 3 and 4 show that the decomposition of lucerne roots under optimum temperature and moisture conditions over a period of 17 days is sufficient not only to eliminate the inhibiting effect of the early stage of humification of lucerne roots but also to increase the yield of barley compared with the treatment "soil+N" and particularly with the control.

These results are convincing evidence of the inhibiting effect on plant growth of lucerne roots at early stages of humification. No doubt a similar

TABLE 121. DEVELOPMENT OF BARLEY AND WEIGHT OF AERIAL PARTS IN EXPERIMENT 4 WITH LIGHT SEROZEM

Treatment	% emergence at the surface	Number of days from sowing to:					Weight of air-dry aerial parts (g)	
		complete emergence	2nd leaf	3rd leaf	tillering	shooting	of 5 plants	of 1 plant
Long period of decomposition (5 months) of lucerne roots	100	5-7	8	12	15-16	20	I* 3.60 II 3.19	0.72 0.64
Short period of decomposition (17 days) of lucerne roots	100	5-6	8	12	15-16	20	I 2.42 II 2.21	0.48 0.44
Undecomposed roots + N	70	none	12	26	not shown	33	I 0.11 II 0.16	0.02 0.03
N	100	5	8	12	15-21	20-23	I 1.77 II 1.53	0.35 0.30
Control	100	5	8	12	15-19	20-23	I 1.40 II 1.54	0.28 0.30

* Replicates.

phenomenon also occurs under natural conditions when crops are sown on poorly decomposed grass sod, particularly at places where the plant residues are concentrated.

Moreover, it should be borne in mind that the intensity of the inhibiting effect depends on the nature of the plant residues—the richer these residues are in readily oxidizable compounds available to micro-organisms, the more marked the effect will be. Instances of this are observed with the decomposition of lucerne roots and also with green manures. With the decomposition of plant residues containing less-easily oxidizable compounds (e.g. grass roots), a less-pronounced inhibiting effect can be expected. In this connexion, a sod consisting of a mixture of grasses and legumes is clearly preferable to a sod of legumes in pure stand.

In order to avoid the inhibiting effect of undecomposed sod on the following crop, it is necessary for the early stage of humification to be completed before the crop is sown. From the experiments described, it can be seen that under favourable temperature and moisture conditions this stage of humification of lucerne roots is completed in about 14 days.

In regions of adequate moisture with autumn ploughing (September—beginning of October) there is time for the early stage of humification to be completed during the autumn and spring periods preceding the sowing of spring cereals.

However, in dry regions and even in regions of variable moisture, if there is a dry autumn and an insufficiently warm spring, with late (October) dates of ploughing the sod and with the sowing of spring cereals in the first half of April, the early stage of humification of plant residues may coincide with the early stages of development of the spring cereals; this will inevitably produce an inhibiting effect.

Therefore, in regions of inadequate moisture, and to some extent also in regions of variable moisture, higher yields of spring cereals are obtained with early autumn or even summer dates of ploughing the sod. In such cases, the early stages of humification of plant residues have time to be completed prior to sowing. This conclusion is also important for the instances when the sod of perennial herbage is turned in, when green manures are ploughed in, and when virgin lands are being reclaimed.

CHANGES IN ORGANIC MATTER RESULTING FROM COMPLEX SYSTEMS OF SOIL IMPROVEMENT

We have already examined the character of the changes which soil organic matter undergoes under various methods of soil improvement—the

ploughing-up of virgin lands, the systematic application of farmyard manure and the introduction of leys.

It would be interesting to find out the changes occurring in the organic part of the soil under long-term measures of soil improvement—systematic grass sowing, the application of organic and mineral fertilizers, liming.

In many works it has been pointed out that as a result of long-term soil improvement podzolic soils become richer in humus, their humus horizon becomes thicker and the podzolic horizon (A_2), on the contrary, becomes thinner and may even disappear (Karpinski, 1933, 1940; Frantesson, 1934; Egorov, 1936, 1939; Gladilovich and Lebedev, 1936; Gnatochkaya, 1938; Tatun'ko, 1938; Sharova, 1940; Smirnova, 1946; Blagovidov, 1948; Garkuscha, 1947, 1951, 1955).

Blagovidov has given the following values (see p. 374) for the humus and nitrogen contents and for the thickness of the A_1 and A_2 horizons in podzolic soils of different degrees of improvement.

These data indicate that in podzolic soils with an increasing degree of improvement the thickness of the humus horizon increases, that of the A_2 horizon considerably decreases and the contents of humus and nitrogen and the pH increase.

Fundamental changes in the organic matter of forest soils with soil improvement were shown by Smirnova (1946), who studied natural forest soils and arable land at the state farm "Dugino" (Smolensk region). The soil-forming rocks and the relief were similar in both cases. The arable soils differed from one another in the degree of improvement attained by correct area allocation of crops and grasses-legumes, by good management, deep ploughing and the application of high rates of farmyard manure. Liming was not carried out.

From a comparison of the structure of the soil profile Smirnova was able to show essential changes in the physical and physico-chemical properties of the soil and particularly the increasing humus content with increasing degree of soil improvement. Smirnova pointed out that with correct management strongly podzolic soils can be brought to the same level of soil improvement as medium podzolic soils with respect to certain physico-chemical properties and agricultural characteristics of the arable layer.

The character of these changes depends directly upon the standard of agricultural technique and in particular upon liming, the use of mineral fertilizers and the enrichment of the soil with organic matter. When inadequate agricultural methods are used, the features characteristic of podzolic soils are retained. In such instances, no substantial differences

Soil	Virgin land	Degree of improvement		
		poor	moderate	good
Heavy loam soils overlying carbonate-free rock:				
Thickness of A_1 horizon (cm)	7-8	12-18	18-22	24-28
Thickness of A_2 horizon (cm)	18-20	15-11	9-5	3-0
% humus in soil	3.0-4.0	1.5-2.0	2.2-3.0	1.0-6.0
% nitrogen in soil	0.12	0.09-0.11	0.12-0.16	0.23-0.26
pH (in KCl extract)	3.5-4.0	4.0-5.2	5.0-5.8	5.8-6.8
Loose sandy loam soils overlying carbonate-free rock:				
Thickness of A_1 horizon (cm)	3-5	14-18	20-24	26-32
Thickness of A_2 horizon (cm)	20-25	10-8	5-2	2-0
% humus in soil	0.5-1.5	1.2-1.8	1.8-2.5	3.0-5.0
% nitrogen in soil	0.06	0.08-0.1	0.12-0.18	0.18-0.24
pH (in KCl extract)	4.0-4.5	5.0-5.5	5.2-6.0	6.0-7.0

are observed in either the humus content or the humus composition when arable soils are compared with soils under forest vegetation (Ponomareva, 1951; Baranovskaya, 1952a; Korotkov, 1957, 1960; Kosheleva and Tolstukhina, 1957; Skalozubova-Golyanovskaya, 1960; Konovalova, 1961; Bel'chikova, 1961).

Examples of the radical changes possible in the state of podzolic soils can be found in the work of Kosheleva and Tolstukhina (1957) and Kaplyuk (1962), who studied the soils of the forest tundra in the northern and central taiga of Western Siberia.

With long-term application of farmyard manure at high rates (90-100 tons per hectare annually for 15-20 years) the soil acidity decreased, and the sum of exchangeable bases increased. At the same time, the humus and nitrogen contents and the humic acid content of the humus were substantially increased. The total humus reserve in the 0-20 cm layer of the soil which received farmyard manure increased from 38 to 118 tons per hectare; this is an increase, in terms of humus carbon, from 22 to 68 tons per hectare. This example is exceptional, because for 20 years, a very large amount of farmyard manure was applied to the soil—about 2000 tons per hectare, that is 500 tons dry matter per hectare, or 250 tons carbon per hectare. Thus, the carbon of the applied farmyard manure amounted to more than ten times the organic carbon reserve of the original soil.

Less pronounced but still appreciable differences in the humus content and composition were recorded by Konovalova (1961) for slightly, moderately and well improved sod-podzolic soils of the Smolensk region.

The work quoted illustrates the "response" of podzolic soils to measures that promote their improvement and in particular the alteration of their humus state. In these soils, the more complete the agrotechnical measures applied, the higher is the degree of improvement.

The detailed effect of long-term reclamation and improvement of chernozems and chestnut soils of the European part of the USSR on their organic matter is given in the monograph by Antipov-Karataev and Filippova (1955). The conclusions drawn from these data agree with the ideas expressed above, characterizing the general uniformity of the processes associated with the transformation of organic substances and the stable state of humus in these soils.

The nature of the change occurring in the humus during the long-term improvement of serozems may be judged from a number of publications. In the present chapter data have been given that indicate the high intensity of microbiological activity in serozems, in particular, the intensity of the mineralization process which prevents the preservation of organic matter in these soils.

However in a number of instances where serozems have been irrigated for a very long time, the humus and nitrogen reserves have increased considerably by comparison with unreclaimed soils. This was because clay particles rich in humus were added to the soil in the irrigation water. The importance of agro-irrigation deposits in the formation of serozem soils has been pointed out by Orlov (1937), Bogdanovich *et al.* (1949), Rozanov (1951), Kostyuchenko (1957), Lagunova (1958) and Dergunov (1959). Evidently these deposits contribute to the increase of both the humus and the nitrogen reserves in the serozems that have been irrigated for many years. For instance, if the humus reserve in the 0–100 cm layer of an unirrigated serozem was 72 tons per hectare, the humus reserves of a serozem that has been irrigated for 20 years was increased to 92.1 tons per hectare and to 159.6 tons per hectare after 500 years irrigation (Kostyuchenko, 1957).

From the examples given for podzolic soils, chernozems, chestnut soils and serozems, it follows that the processes of reclamation and improvement undoubtedly change the organic part of the soil; however, a radical change in the content and composition of soil humus takes a long time. Nevertheless, using various methods of supplementing the reserve of fresh

organic matter, man can establish that biologically-active background which promotes plant growth and the production of high yields.

In the Soviet Union at the present day, great projects such as afforestation, drainage, irrigation and hydro-schemes covering enormous areas will result in fundamental changes in the soil-forming process. The important task with which we are at present faced in the field of soil humus study is to foresee and study the group of problems determining the patterns in humus formation under this fundamental alteration of the soil in order to control its organic-matter regime.

CHAPTER 8

METHODS OF INVESTIGATING SOIL ORGANIC MATTER

IN THIS chapter we shall describe the methods used in our investigations (at the Laboratory of the Biochemistry and Biology of the Soil in the Dokuchaev Soil Institute) on soil organic matter in mineral soils.

Section A includes methods recommended for finding out the general characteristics of soil humus: determination of the content and composition of humus, and of the optical density and coagulation threshold (precipitation) of humic acids that have been isolated from the soil during the determination of humus composition.

In Section B we describe methods for isolating humus substances from the soil and for studying their nature and properties: determination of elementary composition; rapid methods for determining functional groups; fractionation of humus substances by chromatography and electrophoresis.

Section C includes methods for investigating the dynamics of organic substances in the soil: calculation of the aerial mass and roots of plants; the simplified biochemical analysis of fresh and humified plant residues; methods for studying the composition of organic substances in soil solutions.

The listed procedures are not of course the only possible ways of studying soil organic matter; these can be very diverse and will depend on the aims of the investigation. However, information about the methods and procedures we use may be useful for other research workers in this field.

A. METHODS OF DETERMINING THE TOTAL CONTENT AND COMPOSITION OF HUMUS IN MINERAL SOILS

When studying soil humus it is essential that the samples for analysis are carefully prepared. As the preparation methods are generally well-known, we shall merely remind the investigator to be careful in selecting

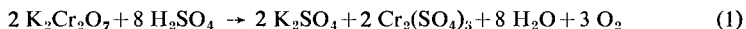
a representative sample and in removing rootlets and other organic residues. If large amounts of half-decomposed plant residues are present (for instance in the upper horizons of meadow and forest soils), fresh and slightly decomposed dead plant residues are first removed and the whole of the remaining sample is taken for analysis. In such instances, the data obtained characterize the organic part of the soil, which includes both humus and incompletely humified plant residues.

The prepared material is passed through a 1 mm mesh sieve, and a sub-sample taken from it for determining the humus composition.

The total carbon and nitrogen contents are determined on an average 3–5 g sample of the material smaller than 1 mm, from which small rootlets have been carefully removed. This sample is ground in a jasper or agate mortar to pass through a 0.25 mm mesh sieve.

THE DETERMINATION OF TOTAL ORGANIC CARBON IN SOILS AND SOLUTIONS BY TYURIN'S METHOD

Tyurin's method (1931, 1936) is a modification of the volumetric determination of soil organic carbon by oxidation with potassium dichromate in strongly acid solution, leading to the formation of CO_2 according to the equation:



The amount of oxygen consumed during the oxidation of organic carbon is calculated from the difference between the amount of dichromate taken and the amount remaining after oxidation; this is determined by titration with a solution of Mohr's salt $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6 \text{H}_2\text{O}$.

If the procedure described below is followed, only about 90 per cent of the organic matter is oxidized when compared with the method of Gustavson (dry combustion). If silver sulphate is used as a catalyst (Komarova, 1933) this figure is raised to 95 per cent.

The analytical procedure is described in detail in many textbooks (Arinushkina, 1961; Bel'chikova, 1960) and so only a brief description of the sequence of operations will be given here.

The sample of air-dried soil, prepared for the determination of the humus content, is weighed on an analytical or technical balance. The size of sample depends upon the expected humus content of the soil and varies from 0.1 to 0.5 g. Tyurin recommends the following weights of sample:

Humus content, %	Sample, g
<hr/>	
10-15	0.05
7-10	0.1
4-7	0.2
2-4	0.3
< 2	0.5

For sandy soils with a low humus content, the sample weight may be increased to 1 g. If the humus content is greater than 15 per cent, this method does not give reliable results because it is not possible to oxidize completely the large amount of organic carbon present.

The soil sample is placed in a dry 100 ml conical flask and Ag_2SO_4 (in powder form) is added from the tip of a knife.¹ 10 ml of 0.4 N potassium dichromate solution is then added to the flask from a burette and the solution is carefully mixed with the soil. A 4 cm diameter funnel is inserted into the neck of the conical flask, and the flask is placed on a hot plate or sand bath. The mixture is heated to boiling point and boiled for exactly 5 minutes.

The flask is then removed from the plate, and the inner and outer surfaces of the funnel and the neck and walls of the flask are carefully washed down with about 10 ml of distilled water. The colour of the liquid after the oxidation is completed should be orange-yellow or greenish-brown. A greenish colour of the liquid indicates insufficient oxidizing agent, and the analysis must be repeated with a smaller sample.

Dichromate mixture unused in the oxidation is titrated with 0.1 M solution of Mohr's salt using phenylanthranilic acid as the indicator, as recommended by Simakov (1957). If the indicator diphenylamine is used (Tyurin's method), the solution must be considerably diluted before the titration; this is avoided with phenylanthranilic acid because a high concentration of sulphuric acid is required during the titration with Mohr's salt. The solution is therefore titrated in the same flask as is used for the digestion. The titration is complete when the colour changes from cherry-violet to bright green; the end point is very sharp.

¹ The use of Ag_2SO_4 in large-scale analysis is ruled out; for comparison with results obtained by dry combustion, Tyurin (1936) recommended the introduction of the experimentally-determined correction factor, 1.17.

Three blank determinations are run at the same time as the batch of soil analyses to establish the volume of Mohr's salt solution equivalent to the dichromate mixture taken for the oxidation of the organic matter. About 0.1 g of calcined soil or pumice is added to the blanks to ensure steady boiling of the liquid and to protect the dichromate mixture from decomposition.

When calculating the analytical results, it should be remembered that the titre of the Mohr's salt solution corresponds with the amount of chromic acid remaining after oxidation of the organic carbon in the soil sample. Tyurin points out that reliable results are obtained when the titre is not less than 20 ml of 0.1 N Mohr's salt solution (when 10 ml of 0.4 N chromic acid is taken for digestion).

The difference between the titres gives the quantity of Mohr's salt equivalent to the chromic acid used for oxidizing the humus in the soil sample.

One gramme-equivalent of carbon is $12.01/4 = 3$ g, so that 1 ml of 0.1 N Mohr's salt solution is equivalent to 0.0003 g of organic carbon or 0.000517 g of humus (it is assumed in calculations that 1 g of carbon corresponds to 1.724 g of humus).

The organic carbon content of the soil is calculated as follows:

$$C \text{ (as per cent of air-dry soil)} = \frac{(a-b) \times 0.0003n \times 100}{c}$$

where a = the volume in ml of Mohr's salt solution used in the titration of 10 ml of 0.4 N $K_2Cr_2O_7$ solution in the blank determination;

b = the volume in ml of Mohr's salt solution used in the titration after oxidation of the humus in the soil sample;

$(a-b)$ = the volume in ml of Mohr's salt solution corresponding to the chromic acid used in oxidizing the humus;

n = a correction for the normality of the Mohr's salt solution;

c = weight of sample in g.

The carbon content of the soil is calculated to an accuracy of 0.01 per cent.

The method described is equally applicable to the determination of organic carbon in soils, in aqueous extracts, and also in the solutions of humus substances isolated during the determination of the humus composition. Additional technical details will be given when this last method is described.

Carbonates do not interfere with the determination of total carbon in the soil and no change in the analytical procedure is necessary. The method does not, however, give reliable results when chlorides, ferrous iron compounds and manganese are present, because part of the chromic acid is used for oxidizing these compounds. If they are present, the humus should be determined by the methods of Knop or Gustavson, in which carbon is determined gravimetrically from the CO_2 liberated during the oxidation of organic matter.

If chlorides are present in the soil, Tyurin's method can only be used if they are removed by washing the sieved (1 mm) soil with distilled water acidified with a few drops of 1 N H_2SO_4 . The soil is washed in beakers by decantation until there is no reaction for the chloride ion. The soil is transferred to a porcelain dish, air-dried on a water bath, and weighed when cool. For subsequent calculation of the carbon content, the ratio of the initial weight of soil to the weight after removal of chlorides and drying must be known.

In the analytical procedure for determining soil carbon the following reagents are required:

1. 0.4 N potassium dichromate solution.

40 g of $\text{K}_2\text{Cr}_2\text{O}_7$, ground in a mortar, are dissolved in 1 litre of distilled water, and the solution filtered. One litre of H_2SO_4 (sp. gr. 1.84) is carefully added to the solution in small portions with stirring so that excessive evolution of heat is avoided; this mixing should be done in a vessel made from heat resisting glass. After cooling the solution is carefully mixed and stored in a flask with a ground stopper.

2. 0.1 N Mohr's salt solution.

The solution contains 40 g of Mohr's salt per litre of water containing 20 ml of H_2SO_4 (sp. gr. 1.84). The salt is dissolved in a small amount of cold distilled water and filtered. The calculated amount of H_2SO_4 is added to the filtrate, the solution made up to volume and carefully mixed. The solution is stored in a bottle provided with a siphon and glass stopcock for delivering the solution to the burette. Because Mohr's salt contains ferrous iron, the titre of the solution is relatively unstable, and should be checked each time before a series of determinations.

3. Phenylanthranilic acid (N-phenylanthranilic acid, $\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}$). The indicator solution contains 0.2 g phenylanthranilic acid in 100 ml of 0.2 per cent Na_2CO_3 solution. The phenylanthranilic acid is

best moistened by grinding it (using a glass rod in a porcelain dish) with a small amount of 0.2 per cent Na_2CO_3 solution until a liquid paste is obtained, and only then adding the remaining sodium carbonate solution with careful stirring.

Total nitrogen in the soil is determined by the Kjeldahl method.

THE DETERMINATION OF THE COMPOSITION OF HUMUS IN MINERAL SOILS BY TYURIN'S METHOD

Tyurin proposed several variants of the method for determining the composition of humus (1940a, 1949, 1951); the 1940 variant, slightly modified, will be described here.

By this method it is possible to characterize differences in the composition of humus from different soil types and also from soils of the same type but with different degrees of improvement.

Tyurin's method specifies that the following groups of organic substances should be isolated successively and determined (as carbon).

1. Substances soluble in ethanol-benzene mixture; in soils this group chiefly includes waxes, resins, and also fats and some humus substances.
2. Substances extracted by dilute mineral acids during the decalcification of soil; this group includes various individual organic compounds — decomposition products from plant and animal residues, and also some strictly humus substances (particularly in podzolic soils, krasnozems and lateritic soils).
3. Humic acids and fulvic acids extracted by 0.1 N NaOH after decalcification of the soil; Tyurin considers that this fraction of humus substances is combined with calcium and mobile forms of R_2O_3 (fraction I of humus substances).
4. Humic acids and fulvic acids extracted during further alternate treatments of the soil with 0.1 N H_2SO_4 and 0.1 N NaOH; these are more strongly combined with the mineral part of the soil, presumably with silicate forms of R_2O_3 (fraction II of humus substances).
5. Humus substances not extracted by the previous procedures — the so-called non-hydrolysable residue of humus substances (humins).
6. Humic acids extracted from a separate sample of non-decalcified soil by 0.1 N NaOH; these are the so-called free humic acids, and those presumably combined with non-silicate forms of R_2O_3 . A com-

parison of the amount of humic acids in this fraction with the total amount extracted after decalcification (see paragraph 3 of this scheme) gives an approximate idea of the amount of humic acid combined with calcium.

The preparation of the soil for determining the humus composition was described at the beginning of Section A. The weight of sub-sample taken depends upon the humus content: when this is 7 per cent or above, the weight should be 10 g; when 4–7 per cent, 20–30 g are taken; when 0.5–3 per cent, 50 g. If the humus content is less than 0.5 per cent, the determination of its composition is not recommended; the data obtained are not considered reliable owing to the small amounts of carbon in the separate fractions of humus substances.

Moderately large soil samples are required for the analysis because the humic acids in fraction I are subsequently used for measuring the optical density and the coagulation (precipitation) threshold, for which large volumes of the solutions are needed. If the optical density and coagulation threshold are not required, the weight of soil sample may be reduced.

*The determination of organic substances extracted by
ethanol–benzene mixture*

The prepared soil sample is placed in an extraction thimble made of dense filter paper and extracted with a mixture of ethanol and benzene (1: 1) in a Soxhlet apparatus heated on a boiling water bath. The extraction is continued until the solvent in the extractor is colourless, which generally takes more than 12 hours.

Before extraction, the receiving flask should be dried to constant weight at 80° C. After the extraction is completed, the solvent in the receiver is driven off on the water bath using a Liebig condenser, and the receiver with the extracted substances is dried for 4 hours in a thermostat and weighed; it is dried for further periods of 2 hours and reweighed, until it reaches constant weight.

The quantity of substance extracted from the soil by ethanolbenzene is given by the difference between the weight of the receiver with extracted substances and the weight of the receiver alone, and is converted to carbon by assuming that the carbon content in this fraction is 72% (this value has been established experimentally).

Martynov (1957) proposed that the weight of substances extracted by ethanol-benzene should be determined in 50 ml weighing bottles. After

most of the ethanol–benzene has been evaporated from the receiver, the remaining extract is transferred whilst hot into a tared weighing bottle rinsing the receiver several times, with fresh hot solvent. The solvent is evaporated from the weighing bottle by heating it on a water bath in a fume cupboard and the bottle and residue dried at 80° C to constant weight. This procedure can only be used when an efficient fume cupboard is available. Martynov's modification considerably shortens the analytical procedure.

The decalcification of soil

This procedure is intended to break (by dilute mineral acids) the link between humus substances and calcium; the humus substances may then be extracted from the soil by alkaline solution. However, it appears that this treatment also affects other associations between humus substances and the mineral part of the soil, such as the non-silicate forms of R_2O_3 .

If a soil contains calcium carbonate, it is decalcified with hydrochloric acid; otherwise, sulphuric acid is used. The method of analysis in these two procedures differs slightly.

The decalcification of soil with H_2SO_4 . This procedure is used for podzolic soils, krasnozems, chernozems free from carbonates, chestnut soils, and other soils.

At the end of the ethanol–benzene extraction, the thimble containing the soil is transferred from the extractor to a porcelain dish under a hood, where it is opened and dried at room temperature until the smell of solvent has disappeared. The soil is then quantitatively transferred to a beaker and 600–800 ml 0.05 N H_2SO_4 are added.

Throughout the day, the contents of the beaker are repeatedly stirred with a rubber-tipped glass rod. Rootlets floating on the surface are removed with a piece of filter paper or a small sieve. Next day, the settled clear solution is filtered off by suction through a glass crucible (Porosity No. 3) into a Bunsen flask, immersing the crucible in the solution above the settled soil and gradually lowering it as the solution is sucked off. The settled soil must not be disturbed. Soils with a low calcium content (podzolic soils, krasnozems) are treated two or three times with acid; with chernozems, chestnut soils and others with a high exchangeable calcium content, the treatment is continued until there is no reaction for calcium in the filtrate. The base of the crucibles becomes gradually blocked with clay

particles; the crucibles are periodically cleaned by washing over a Bunsen flask (with vacuum) successively with saturated $K_2Cr_2O_7$ in concentrated H_2SO_4 , 40% NaOH and hot water.

The separate portions of acid solution are combined, carefully evaporated to small volume (250–500 ml; the solution must not boil) and transferred to a volumetric flask. An aliquot (20–25 ml) is pipetted into a 100 ml conical flask and neutralized by adding 1.0 N NaOH drop by drop (Tyurin recommends dry powdered Na_2CO_3 for this purpose). This solution is evaporated to dryness on a boiling water bath without allowing the precipitate to darken. Carbon is then determined by Tyurin's method; to ensure steady boiling of the dichromate mixture, a small amount of calcined soil or pumice is added from the tip of a knife.

For the subsequent extraction of humus substances, the whole sample of decalcified soil (in a moist condition) is used. It is not necessary to wash the soil free from sulphuric acid.

The decalcification of soil with HCl. This procedure is for soils containing calcium carbonate. As before, the soil sample is decalcified after extraction with ethanol–benzene mixture. The soil sample is quantitatively transferred to a beaker, and if a large amount of carbonate is present (for instance, in serozems) this is destroyed by a preliminary treatment with 0.5 N or 1.0 N HCl. The soil is decalcified with 0.05 N HCl, following the same procedure as with H_2SO_4 (see above). After calcium has been removed, the soil is washed with 0.1 N H_2SO_4 until free from Cl ion.

When soil is decalcified with HCl solution, the acid filtrates are discarded, because a direct determination of carbon by Tyurin's method in these filtrates is impossible; dichromate mixture would be used up in oxidizing not only organic matter but also chlorides. The carbon content of organic substances dissolved in the acid extract is determined indirectly from the difference between the carbon content of the soil before and after decalcification.

However, to avoid the complicated calculation of carbon in this determination, and estimation of the soil sample for subsequent isolation of humus substances, the analytical scheme can be simplified by omitting the determination of the amount of carbon extracted during decalcification. In carbonate soils, the amount of carbon extracted is small and not characteristic. With such soils, the Cl ion is carefully removed from the soil after decalcification by washing the soil first with 0.05 N H_2SO_4 and then with distilled water. The whole soil sample is taken, without drying, for the extraction of humus substances.

The isolation from the soil of humus substances combined with mobile forms of R_2O_3 (fraction I of humus substances)

The decalcified soil in a beaker is covered with 0.1 N NaOH solution and left for 4–5 hours with occasional stirring. To coagulate the clay fraction, about 50 g of finely ground sodium sulphate are added and the solution is stirred vigorously for 8–10 minutes until the salt is dissolved. The hydrated salt $Na_2SO_4 \cdot 10 H_2O$ gives better results than anhydrous Na_2SO_4 .

The addition of sodium sulphate gives clear alkaline extracts which are essential in this analysis. After settling for 18–20 hours, the dark-coloured solution of humus substances is drawn off through a porosity No. 4 crucible in the same way as during decalcification of the soil.

If the alkaline solutions remain cloudy (when, for instance, working with soils of heavy mechanical composition) they must be centrifuged and the precipitated soil returned quantitatively to the beakers.

Treatment of the soil with 0.1 N NaOH is repeated until the alkaline solution is only faintly coloured. With podzolic soils and krasnozems, three to four treatments are necessary for a complete extraction, whereas with chernozems five to eight and sometimes more are required.

Alkaline soil extracts contain humic acids and fulvic acids. These are separated immediately after filtering each portion: the clear alkaline solution is transferred to a beaker and 4 ml H_2SO_4 (sp. gr. 1.84) added for each 500 ml of extract (pH of the solution 2–3). The solution is stirred and heated on a hot plate or sand bath to 80° C (the solution must not be boiled or concentrated by evaporation).

During acidification and heating, humic acids coagulate; on cooling they settle to the bottom of the beaker as a dark precipitate and fulvic acids remain in the solution, which has a yellow or orange colour.

To complete the precipitation of the gel of humic acids, the beaker is set aside until the following day. The clear solution of fulvic acids is carefully drawn off through a porosity No. 4 crucible without disturbing the precipitate of humic acids.

The precipitates of humic acids from individual extractions are combined and washed two or three times with distilled water to remove SO_4 ion, the gel being allowed to settle well. Centrifuging may be used during this washing procedure; if the volume of precipitate is large, it may be distributed among several tubes.

When most of the electrolyte has been removed (as indicated by the appearance of a brown colour in the liquid), the gel is dissolved in 0.02 N

NaHCO_3 and transferred to a volumetric flask of suitable size for the volume of precipitate. The solution of sodium humate should be perfectly clear; if it is cloudy it is centrifuged or set aside for 7–10 days before drawing off the supernatant.

For the carbon determination, an aliquot of 5–25 ml (depending on the intensity of the colour) is taken from the solution of sodium humate and transferred to a 100 ml conical flask. The solution is neutralized with a few drops of concentrated H_2SO_4 until the initially clear solution becomes slightly cloudy, and evaporated to dryness on a water bath. The carbon content is determined by Tyurin's method.

The carbon content of fulvic acids is determined as follows. The fulvic acid extracts separated from the humic acid gel are combined and, without neutralization, are carefully concentrated in a beaker on a hot plate or sand bath (the solution must not boil), until the volume is 200–500–1000 ml depending on the intensity of the colour. A brown flocculated precipitate sometimes appears during the concentration of fulvic acids; it is a condensation product and is not filtered off but left in the fulvic acid solution.

When crystals of sodium sulphate separate, the solution is cooled and decanted. The crystals are washed several times with distilled water and the washings are added to the main batch of fulvic acid solution; the crystals are discarded. The cloudiness which sometimes appears in the solution of fulvic acids during cooling does not interfere with the carbon determination.

The concentrated solution of fulvic acids is transferred to a volumetric flask, carefully mixed, and an aliquot taken for the carbon determination; the remainder of the procedure is the same as for humic acids. When the aliquot is being evaporated, crystals of sodium sulphate precipitate on the bottom of the flask, but these do not interfere with the subsequent carbon determination by Tyurin's method.

The separation of humus substances bound more strongly to the mineral part of the soil (fraction II of humus substances)

Humus substances presumed bound to stable silicate forms of R_2O_3 are extracted by treating the soil alternately with 0.1 N H_2SO_4 and 0.1 N NaOH solutions.

The procedure is as follows. When the extraction of fraction I is completed, the alkali remaining in the beaker is neutralized with H_2SO_4 (sp. gr. 1.84) and the soil well covered with 0.1 N H_2SO_4 solution; the mixture

is left for 24 hours with occasional stirring. The following morning the clear acid solution is removed by suction through a porosity No. 3 crucible and discarded. The soil is covered with 0.1 N NaOH solution and occasionally stirred; at the end of the day dry sodium sulphate is added and the remaining procedure is the same as that used for extracting fraction I of humus substances. The alternate treatment of the soil with acid and alkali is repeated several times until humus substances are no longer separated.

The carbon contents of the humic acids and fulvic acids are determined by the method described above for fraction I.

The determination of carbon in the soil residue

When the alternating treatment is completed, the slurry in the beaker is slightly acidified with 1 N H_2SO_4 and Na_2SO_4 is removed by filling the beaker with distilled water and mixing the contents. The settled clear solution is drawn off through a porosity No. 3 crucible and discarded.

The washing is continued until the liquid remains cloudy after leaving 24 hours for the soil to settle; this indicates that Na_2SO_4 has been removed. The suspension and the soil are transferred from the beaker to a weighed 10 cm porcelain dish and evaporated to dryness on a boiling water bath; after leaving for 24 hours to reach air-dry condition, the dish is weighed. The ratio of the weight of soil residue to the weight of soil taken for determining the humus composition is necessary for further calculations.

After weighing, the soil is ground in a porcelain mortar to pass a 0.25 mm mesh sieve and stored in a tightly stoppered tube to prevent change in its moisture content. Sub-samples are taken from this tube for determining carbon in the residue, as before, by Tyurin's method.

While estimating the fractional composition of humus, total nitrogen is determined by Kjeldahl's method on the original soil and on the residue after the extraction of humus substances.

Calculations

The carbon content of each fraction of the humus is expressed as a percentage both of the weight of soil sample, and of the total organic content of the soil. The sum of organic carbon in all the fractions of humus substances extracted should total 90–98 per cent of the total carbon in the soil sample, if all the extracted fractions have been accounted for quantitatively. If the sum is less than 90 per cent or exceeds 100 per cent,

the analysis must be repeated. The nitrogen content is expressed similarly.

We now illustrate these calculations for a gray forest soil; the carbon content of the original soil was 1.36 per cent.

1. The carbon content of organic substances soluble in ethanol-benzene

Weight of soil taken for humus composition analysis	30 g
Weight of substances extracted from this sample by ethanol-benzene	0.03191 g
Carbon content of this fraction (assuming that the C content of substances in this fraction = 72%)	0.02298 g
Carbon content of substances extracted (as % of the weight of soil)	0.08
Carbon content of substances extracted as % of total soil carbon (1.36%)	5.9

2. The carbon content of organic substances extracted from the soil during decalcification. An example of the calculation is given only for the method in which the soil is decalcified with sulphuric acid; this method is used for all soils except carbonate soils. As pointed out above, the latter are decalcified with HCl, and the amount of organic matter extracted in this way is not taken into account.

Carbon in the acid extract collected during decalcification of the soil with H_2SO_4 is determined directly in the extract (after careful evaporation, see the section "The decalcification of soil with H_2SO_4 ") and calculated as follows (Table 122).

TABLE 122. CALCULATION OF THE AMOUNT OF ORGANIC MATTER CARBON EXTRACTED FROM THE SOIL DURING DECALCIFICATION WITH H_2SO_4

Weight of soil taken for determining humus composition g	Total volume of acid solution after evaporation ml	Aliquot of solution taken for carbon determination ml	Weight of soil corresponding to the volume taken g	Carbon in the aliquot taken g	Organic matter carbon in acid solution	
					% soil weight	% total soil organic C
30	100	20	6	0.00562	0.09	6.6

3. *The carbon content of humic acids and fulvic acids (Fractions I and II).* The calculations are the same, irrespective of the method used for decalcification, because the whole sample taken for determining the humus composition is used for extracting the humus substances (Table 123).

TABLE 123. CALCULATION OF HUMIC ACID AND FULVIC ACID CARBON

Weight of soil taken for determining humus composition g	Total volume of humic acid or fulvic acid solution ml	Aliquot of solution taken for carbon determination ml	Weight of soil corresponding to the volume taken g	Carbon in the aliquot taken g	Humic acid or fulvic acid carbon	
					% soil weight	% total soil organic C
30	250	10	1.2	0.00364	0.30	22.1

4. *The carbon content of the soil residue after the extraction of humus substances*

Weight of soil taken for humus composition analysis	30 g
Weight of air-dry residues	28 g
Weight of residue corresponding to 100 g original soil	93.3 g
Weight of residue taken for C determination	0.5 g
Weight of carbon determined in 0.5 g residue	0.0022 g
Carbon in soil residue (as % of original soil)	$\frac{0.0022 \times 93.3}{0.5} = 0.41$
Carbon in soil residue (as % of total soil C)	30.1

After calculating the carbon contents of the individual fractions of humus substances separated during the analysis of humus composition, the results are summarized in a table (Table 124).

In addition to the carbon contents of the individual fractions of humus substances, the ratio of humic acid carbon to fulvic acid carbon is also given in the table. This ratio has characteristic values for different soil types and sub-types.

From experience with many soils, we consider that differences in the contents of the fractions of humus substances are only reliable when they exceed 3–4 per cent of the total humus substances determined.

*The determination of free humic acids and humic acids combined
with mobile forms of R_2O_3* ¹

This determination is included in Tyurin's scheme of analysis for humus composition; alternatively, the method can be used separately, for example, in studying the dynamics of mobile humic acid forms in soils of different utilization.

The soil is prepared for analysis in the same way as for the determination of humus composition. Five grammes of air-dry soil are placed in a 250 ml conical flask and at the end of the day covered with 100 ml of 0.1 N NaOH prepared with CO₂-free water (prepared by boiling distilled water for 2 hours). Absorption of CO₂ from the air is prevented by inserting a rubber stopper tightly into the neck of the flask. The flask is shaken to ensure that the alkali completely and uniformly wets the soil and is left for 15–16 hours at laboratory temperature (18–20° C).

The amount of humic acid extracted is considerably influenced both by the length of time that the soil is in contact with alkali and also by the temperature (Nered, 1957²); the same conditions should therefore be used for each analysis.

Next morning the contents of the flask are mixed and transferred to a 9–10 cm funnel containing a simple paper filter that has been inserted into a cone of fine filter paper. Usually the first portions of the filtrate are cloudy, so the extract is at first filtered into the conical flask used in extracting the soil with 0.1 N NaOH. When the filtrate becomes clear, 60–70 ml are collected in a clean dry flask and the filter and soil discarded. To precipitate the humic acids, 50 ml of the clear solution are taken in a beaker and H₂SO₄ (sp. gr. 1.84) is added drop by drop until the solution begins to appear cloudy (the beginning of precipitation of the humic acid gel); an excess of acid should be avoided. The solution is carefully heated (not higher than 80° C) for 30 minutes. Next day the acid solution is filtered, using a small funnel and a filter, without disturbing the gel which has settled to the bottom of the beaker. The gel is transferred to the same filter and washed twice with 0.02 N H₂SO₄; the filtrate and washings are discarded.

¹ The method is described by the following authors: Tyurin (1949); Tyurin and Naidenova (1951); Kononova, Pankova and Bel'chikova (1949); Pankova (1960).

² Nered, Z. A. (1957) Methods of determining mobile humic acids, *Byul. vsesoyuz. nauch. — issled. Inst. Kukuruzy* (4).

TABLE 124. SUMMARY OF DATA ON THE COMPOSITION OF SOIL HUMUS

Soil depth of sampling cm	Organic C, % soil weight	Humus (C × 1.724)	Total N, % soil weight	C : N ratio of original soil	In the composition of humus*										humic acid/fulvic acid ratio	C : N ratio in residue	Total C of all fractions % original soil carbon
					Substances extracted by ethanol-benzene	Substances extracted during decalcification	humic acids		fulvic acids			residue					
							frac-tion I	frac-tion II	Total	frac-tion I	frac-tion II	Total	C	N			
Gray forest soil 20-25	1.36	2.34	0.18	7.56	0.08	0.09	0.30	0.08	0.38	0.26	0.10	0.36	0.41	0.06	97.1		
	5.9				6.6	22.1	5.9	28.0	19.1	7.4	26.5	30.1	33.3				

* In the numerator the carbon content of the fractions of organic matter, as % of air-dry original soil; in the denominator the carbon content of the fractions of organic matter, as % of total soil organic C.

The funnel containing the precipitate of humic acids is placed over a 50 ml volumetric flask and the gel dissolved as follows.

Hot 0.02 N NaOH is added in small portions to the gel on the filter; the solution of sodium humate is collected in the volumetric flask. Gel sticking to the walls of the beaker is dissolved by washing several times with hot 0.02 N NaOH solution; the washings are added to the solution in the volumetric flask. After cooling, the contents of the flask are made up to volume with distilled water and carefully mixed. Humic acid carbon in this solution is determined by Tyurin's method. For convenience of calculation, 20 ml aliquots, corresponding to 1 g of soil, are taken for the determination.

The amount of carbon in free humic acids and humic acids combined with mobile forms of R_2O_3 is calculated as a percentage of the soil weight and as a percentage of the total soil carbon.

TABLE 125. CALCULATION OF FREE HUMIC ACID AND MOBILE HUMIC ACID CONTENTS

Organic C % soil weight	Weight of soil taken for analysis g	Volume of 0.1N NaOH taken for extraction of humus substances ml	Weight of soil (g), corresponding to the volume of sodium humate (20 ml) taken for carbon determination	Amount of carbon in the volume taken g	Carbon of mobile humic acids	
					% air-dry soil	% total soil C
1.36	5	100	$\frac{5 \times 50 \times 20}{100 \times 50} = 1.0$	0.0015	0.15	11.0

The difference between the amount of humic acids extracted from the soil after decalcification (fraction I) and the amount extracted by the treatment described in this section gives an approximate measure of the humic acids combined with calcium. In our example, this is equal to $22.1 - 11.0 = 11.1$ per cent of the total soil carbon (Table 125).

RAPID METHOD OF DETERMINING THE COMPOSITION OF HUMUS IN MINERAL SOILS

This method, which is based on the use of sodium pyrophosphate for extracting humus substances from the soil, has been developed jointly with Bel'chikova (1961).

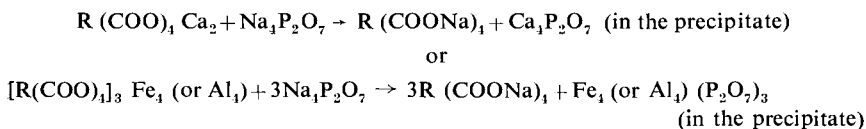
Solutions of sodium pyrophosphate and of the neutral salts of certain organic acids such as sodium oxalate, citrate and tartrate, form insoluble

precipitates or soluble complexes with calcium, iron, aluminium and some other polyvalent cations with which humus substances are combined in the soil.

Sodium pyrophosphate is convenient because it extracts organic matter quickly (in 10–12 hours). In contrast to when NaOH is used, neither the preliminary soil decalcification with dilute HCl or H₂SO₄, nor repeated extraction of the soil with the solution, substantially influence the yield of humus substances, even when large amounts of exchangeable calcium or carbonates are present.

The pH of the sodium pyrophosphate solution is very important; raising the pH from 7.0 to 9.5 increases the yield of humus substances. Our investigations have shown that the greatest quantity of humus substances is extracted by a mixture of sodium pyrophosphate and NaOH having a pH of about 13 (see Table 4). A single treatment of the soil with this solution gives a yield of humus substances similar to the quantity of humic acids and fulvic acids obtained by Tyurin's method (repeated extraction of a previously decalcified soil with 0.1 N NaOH). With some variation, a similar humic acid/fulvic acid ratio is obtained from both methods.

Apparently, when the mixture Na₄P₂O₇ and NaOH is used, calcium, iron and aluminium are replaced by sodium, so that soluble sodium humates and fulvates and insoluble pyrophosphates of the corresponding cations are formed. The reaction may be represented as follows:



It may therefore be assumed that treatment of the soil with the Na₄P₂O₇–NaOH mixture extracts humus substances combined with calcium as well as with non-silicate forms of iron and aluminium.

These two fractions may be differentiated if the amount of humus substances extracted from non-decalcified soil by 0.1 N NaOH solution is also determined.

If this latter method isolates humus substances that are free or combined with non-silicate forms of R₂O₃, then comparison of this amount with the quantity of humus substances extracted with the Na₄P₂O₇–NaOH mixture will give an indication of the amount combined with calcium.

Thus, the rapid method proposed by us for determining the composition of humus avoids the lengthy (particularly with carbonate soils) decalcification of the soil and the repeated extractions with 0.1 N NaOH solution.

The soil is prepared for analysis by the method used when determining the humus composition by Tyurin's scheme. Organic carbon in the original soil and in the solutions of humus substances is determined by Tyurin's method and total nitrogen by Kjeldahl's method.

The composition of humus is determined by the rapid method as follows.

Extraction of humus substances from soil by sodium pyrophosphate—sodium hydroxide mixture

Five grammes of the soil sample prepared for the determination of humus composition are taken in a 250 ml conical flask and at the end of the day, 100 ml of freshly-prepared sodium pyrophosphate-sodium hydroxide mixture are added (the solution contains 44.6 g $\text{Na}_4\text{P}_2\text{O}_7$, 10 H_2O and 4 g NaOH per litre, that is the concentration of the solution is 0.1 M with respect to pyrophosphate and 0.1 N with respect to NaOH; the pH of the mixture is about 13).

The flask is tightly stoppered with a rubber bung to prevent the solution from taking up atmospheric CO_2 ; the contents are carefully mixed and left to stand until next morning. A longer reaction period between the soil and solution does not increase the yield of humus substances above that obtained after 16–18 hours.

Next morning the contents of the flask are again carefully mixed and the whole solution and soil transferred to a funnel which contains an ordinary filter paper of 15–17 cm diameter inserted into a cone of fine filter paper (7–9 cm diameter). The filter papers must be dry.

If the filtrate is cloudy it should be returned to the filter; the clear filtrate is collected in a dry flask. If the filtrate continues to be cloudy, it is filtered a second time through the same filter containing the soil. For soils with a high humus content (e.g. chernozems), it is only necessary to filter 50–60 ml of extract, but for soils with lower humus content, the whole extract should be filtered.

Instead of filtering through paper, the extract may be separated from the soil by centrifuging. In either case, it is essential that the extracts are clear. We do not add a coagulating agent.

The soil residue on the filter is not required for further analysis and is discarded.

Total organic carbon and humic acid carbon are determined in the extract by the following procedures.

The determination of total organic carbon in the extract

The volume of extract taken for determining the organic carbon depends on the intensity of its colour. If the extracts are dark-coloured, 2–5 ml of extract are sufficient, but if the extracts are light-coloured, 10–15 ml should be taken.

The aliquot is pipetted into a 100 ml conical flask and neutralized by adding H_2SO_4 drop by drop until a slight cloudiness appears in the solution. The flask is then placed on a boiling water bath until its contents are evaporated to dryness. Organic carbon is determined by Tyurin's method; some calcined pumice or loess soil is added from the tip of a knife to ensure steady boiling and to eliminate overheating of the liquid.

The contents of the flask are diluted with 5–10 ml distilled water and titrated with 0.1 N Mohr's salt solution, using phenylanthranilic acid as the indicator.

Organic carbon in the extract must be determined in duplicate; the carbon content is calculated both as a percentage of soil weight and as a percentage of the total organic carbon in the original soil (see Table 126).

The determination of humic acid carbon in the extract

An aliquot of the extract (25 ml for soils with a high humus content and 40–50 ml for moderate and low humus contents) is pipetted into a beaker of appropriate volume; the humic acid gel is coagulated by adding H_2SO_4 (sp. gr. 1.84) drop by drop, stirring the solution with a glass rod, until a cloudiness appears in the solution, which occurs at pH 2.0–3.0. Approximately 0.2–0.5 ml of H_2SO_4 are necessary; an excess of acid must be avoided. After carefully stirring the contents of the beaker with the glass rod, the beaker is heated to not more than 80° C for 30 minutes and left at room temperature overnight to complete the precipitation of the humic acid gel. Next morning the extract is filtered in a small funnel through a fine 7 cm diameter filter previously moistened with 0.05 N H_2SO_4 . First the acid solution is transferred from the beaker to the filter and then the humic acid gel. The precipitate on the filter is washed several times with cold 0.05 N H_2SO_4 until the filtrate is colourless (at the beginning of the washing, the filtrate is usually coloured yellow by fulvic acids). The acid solution and washings are discarded and the funnel with the filter and precipitate of humic acids is inserted into the neck of a volumetric flask (capacity 25–100 ml, depending on the volume of the precipitate). The precipitate is dissolved in warm 0.05 N NaOH solution.

Small amounts of the NaOH solution are first added to the beaker in which the humic acids were precipitated so that any precipitate sticking to its sides is dissolved; the solution is then transferred to the filter. The filter is washed with the same solution until the gel of humic acids is completely dissolved; this is indicated by the absence of colour in the filtrate. The solution of sodium humate in the volumetric flask is cooled to room temperature and made up to volume with distilled water. 5–20 ml (depending on the intensity of the colour of the solution) are taken for determining the carbon, using the same analytical procedure as is used for determining total carbon in the extract. The humic acid C is calculated both as a percentage of soil weight and as a percentage of total organic carbon in the original soil (see Table 127).

The determination of fulvic acid carbon in the extract

The amount of fulvic acid carbon (or more correctly, carbon of the organic substances remaining in the acid solution after the humic acids have been precipitated from the extract) is found by subtracting the humic acid carbon from the total organic carbon in the extract. The fulvic acid C is calculated both as a percentage of soil weight and as a percentage of total organic carbon in the original soil.

The determination of carbon in the soil residue

The amount of carbon left in the soil residue after extracting humus substances with the sodium pyrophosphate–sodium hydroxide mixture is found by subtracting the organic carbon in the extract from the organic carbon in the original soil.

As can be seen from the foregoing, we determine the amount of humus substances extracted by the pyrophosphate–hydroxide mixture from the yield of carbon. These analyses may be accompanied by determinations of the nitrogen content of the original soil, of the extract and of the humic acids. The amount of nitrogen in the fulvic acids and in the soil residue is found as in the case of carbon, by the difference between the total N content of the original soil and the N content of the whole extract.

The determination of nitrogen requires a larger quantity of extract, and it is more convenient to run parallel series of samples rather than increase the soil samples and correspondingly the volume of solution. Determinations of N, as with C, are done in duplicate.

In tables 126 and 127, examples are given of the calculation when total organic carbon and humic acid carbon are being determined. The calculation is always the same, regardless of the type of soil.

If chlorides are present in the soil, they must be removed before determining the humus composition, because they are extracted by the $\text{Na}_4\text{P}_2\text{O}_7\text{--NaOH}$ mixture and so falsify the determination of carbon in extract by Tyurin's method. The procedure for removing chlorides from the soil was described earlier in this chapter in the section "The determination of the total organic carbon in soils and solutions by Tyurin's method."

TABLE 126. CONTENT OF TOTAL ORGANIC CARBON IN THE EXTRACT

Soil	C % original soil	Weight of soil taken for analysis g	Volume of pyrophos- phate mixture taken for ex- traction of humus substan- ces ml	Volume of extract (3) taken for C de- termination ml	Weight of soil cor- responding to the volume taken (4) g	C in soil sample (5) g	Organic C in extract	
							% soil weight	% orga- nic C of ori- ginal soil
	1	2	3	4	5	6	7	8
Ordinary chernoz- em	5.00	5	100	2	0.1	0.00249	2.50	50

TABLE 127. CARBON CONTENT OF HUMIC ACIDS IN THE EXTRACT

Weight of soil taken g	Volume of pyrophos- phate mixture taken for extrac- tion of humus substan- ces ml	Volume of extract taken for precipi- tation of humic acids ml	Final vo- lume of Na hu- mate ml	Aliquot of ex- tract (4) taken for C deter- mination ml	Weight of soil cor- respond- ing to the volume (5) g	Carbon in soil sample (6) g	Organic C in extract	
							% soil weight	% orga- nic C of ori- ginal soil
1	2	3	4	5	6	7	8	9
5	100	20	100	10	0.1	0.00185	1.85	37.0

Supplementary determinations

We consider it is advisable to supplement the analysis of humus composition described above by the following determinations, using separate soil samples.

(a) The determination of the organic carbon passing into solution when the soil is treated directly with 0.1 N H_2SO_4 (see Ponomareva, 1957). This determination indicates the solubility of the soil organic matter in mineral acids, which is a particular characteristic of podzolic soils, krasnozems and lateritic soils.

A sample of the soil (passed through a 1 mm mesh sieve) is placed in a 250 ml conical flask and covered with 200 ml of 0.1 N H_2SO_4 ; the soil and acid are well mixed and left for 20–24 hours. Next day the sulphuric acid extract is filtered into a 500 ml volumetric flask. The soil is transferred from the conical flask to the filter and washed with 0.1 N H_2SO_4 , and the total volume of the solution made up to 500 ml.

For the carbon determination, a 50 ml aliquot is neutralized with sodium carbonate, evaporated to dryness and digested with dichromate mixture. The results of the carbon determination are expressed both as a percentage of the soil weight and as a percentage of the soil organic carbon.

(b) Free humic acids and humic acids combined with mobile forms of R_2O_3 are determined by extracting the non-decalcified soil with 0.1 N NaOH. The analytical procedure has been described above. The difference between the total humic acids extracted from the soil by $\text{Na}_4\text{P}_2\text{O}_7$ –NaOH solution and humic acids, free and combined with mobile forms of R_2O_3 , indicates the quantity of humic acids combined with calcium.

It is considered advisable to accompany the determination of humus composition by a characterization of the nature and properties of the humus substances, which, as can be seen from the data in Chapters 2 and 6, vary considerably from soil to soil. For this purpose, the optical density of the humus substances and their behaviour towards electrolytes are determined.

The basis of this method and the technical details of the determinations are described below.

In conclusion, Table 128 gives results for the composition of humus, obtained by the rapid method of extracting humus substances with $\text{Na}_4\text{P}_2\text{O}_7$ –NaOH solution. The table also includes results from the supplementary determinations: the carbon content of the substances extracted by 0.1 N H_2SO_4 , the humic acids extracted from non-decalcified soil by 0.1 N NaOH, and also the ratio of E_4 to E_6 ; this ratio has been calculated from the optical densities at two wavelengths, 465 m μ and 665 m μ .

THE DETERMINATION OF THE OPTICAL DENSITY OF HUMUS
SUBSTANCES

The optical properties and, in particular, the optical density of humus substances depend on their chemical structure. It has been suggested that the optical density of organic substances is directly proportional to their conjugated double bond content (Cherkesov, 1957¹). Correspondingly, the optical density of alkaline solutions of humic acids with equal carbon content characterizes the ratio of the carbon in the aromatic net to the carbon in the side radicals.

The optical density is determined with a spectrophotometer in the visible or ultraviolet region of the spectrum. It is characterized by the absorption of light passing through a 1 cm layer of the substance investigated and expressed by the formula $D = \log (I_0/I)$, where D is the optical density, I_0 the intensity of the incident light and I the intensity of the light after passing through the solution. D has the same value as the extinction coefficient E (for the same concentration in solution of the substance investigated) calculated for a 1 cm layer.

These properties were first determined, during the study of humic acids isolated from peat, coal and various soils, by Oden (1919) and later by Hock (1937, 1938), Frömel (1937), Springer (1938), Davydov (1941) and Aleshin and Zhupakhina (1950). During comparative studies of the chemical structure and the optical properties of humic acids of different origins, it was found that "younger" humic acids, in a chemical sense, have a lower optical density than more "mature" humic acids (Trocmé and Barbier, 1947; Kononova and Bel'chikova, 1950; Scheffer and Welte, 1950a, b; Kukhareenko, 1953b; Kumada, 1955b; Kononova, 1956; Larina and Kasatochkin, 1957; Orlov, 1959, 1960, etc.). This general observation is due to the high condensation of the aromatic carbon net in the "mature" humus and to the predominance of side chains in the "young" humic acids.

We have isolated preparations of humic and fulvic acids from various soils and determined their optical density; the results are shown in Fig. 10.

We make similar measurements when determining the composition of humus, using the humic acid fraction extracted by 0.1 N NaOH from non-decalcified soil (Tyurin's determination of humus composition) or by $\text{Na}_4\text{P}_2\text{O}_7$ -NaOH solution (the rapid method of Kononova and Bel'chikova).

¹ Cherkesov, A. I. (1957) Displacement of the maxima of absorption spectra of some organic reagents during their ionization and interaction with metal ions, *Optika Spektrosk.*, **2** (6), 825.

TABLE 128. COMPOSITION OF HUMUS FROM ORDINARY CHERNOZEM*

Depth cm	C in original soil %	Organic C extracted by 0.1 N H ₂ SO ₄	Organic C extracted by Na ₄ P ₂ O ₇ -NaOH	Humic acid C	Fulvic acid C	Humic acid C Fulvic acid C	E ₄ :E ₆	Total amount of humic acids		C of soil residue
								free and combined with R ₂ O ₃	combined with Ca	
	1	2	3	4	5 (3-4)	6	7	8	9 (4-8)	10 (1-3)
0-20	5.00	0.15 3.0	2.50 50.0	1.85 37.0	0.65 13.0	2.85	3.4	0.17 3.4	1.68 33.6	2.50 50.0

* In the numerator - carbon, % of soil weight; in the denominator — carbon, % of total organic C in original soil.

The preparation of humic acid solutions starts at the stage where the gel is washed into a beaker or centrifuge tube and dissolved in 0.02 or 0.05 N sodium bicarbonate solution, the volume of which depends on the volume of the gel. The sodium humate is transferred to a volumetric flask and made up to volume with the same sodium bicarbonate solution. The solutions are left in closed flasks for 4–5 days; during this time the pH stabilizes near the range 8.2–8.8.

TABLE 129. DEPENDENCE OF OPTICAL DENSITY OF HUMATE SOLUTIONS* ON pH

Filter wavelength m μ	pH of solution			
	7.2	8.8	9.8	13.0
726	0.49	0.50	0.50	0.58
665	0.72	0.77	0.78	0.84
619	0.94	1.01	1.01	1.12
574	1.32	1.38	1.40	1.48
533	1.70	1.70	1.76	1.89
496	2.07	2.10	2.14	2.30
465	2.45	2.50	2.55	2.65

* Carbon concentration in humate solutions equals 0.136 g/litre.

It is essential that the humate solutions are clear before the optical density is determined. The pH and the concentration of carbon in the sodium humate solutions, are important when optical properties are being determined (Tables 129 and 130); good values are obtained at pH 7.2–9.8 and when the concentration of C in the humate is 0.136–0.140 g per litre of solution.

Carbon is determined in the sodium humate solutions by the usual procedure (see Tyurin's or Kononova and Bel'chikova's determination of humus composition). The solutions are then brought to a given carbon concentration; we have found by experience that 0.133–0.138 g carbon per litre is convenient. It is therefore necessary to determine by how much the carbon concentration in the original humate solution exceeds the chosen value, and then the original solution is diluted to the same carbon level by adding a calculated amount of distilled water.

TABLE 130. DEPENDENCE OF OPTICAL DENSITY OF HUMATE SOLUTIONS ON CARBON CONCENTRATION

Filter wavelength m μ	Carbon concentration g/litre			
	0.136	0.140	0.150	0.198
726	0.49	0.52	0.53	0.78
665	0.72	0.75	0.81	1.14
619	0.94	0.98	1.08	1.48
574	1.32	1.35	1.43	1.96
533	1.70	1.73	1.80	2.49
496	2.07	2.15	2.25	3.00
465	2.45	2.50	2.70	3.50

The solution is diluted as follows: a suitable volume is pipetted into a dry flask and the calculated amount of distilled water added. The solution is carefully mixed and tightly closed to prevent evaporation.

TABLE 131. CALCULATION OF THE DILUTION OF SODIUM HUMATE SOLUTIONS

Soil	Carbon in one litre humate solution g	Chosen carbon concentration of humate solution g/litre	Ratio of carbon concentration in investigated humate solution to chosen concentration	Dilution of investigated humate solution		Total volume of humate solution after dilution ml
				Volume of humate solution taken ml	Volume of added distilled water ml	
Strongly podzolic soil	0.1717	0.136	$\frac{0.1717}{0.136} = 1.26^*$	100.0	26.0	126.0
Ordinary chernozem	0.4259	0.136	$\frac{0.4259}{0.136} = 3.13^*$	50.0	106.5	156.5

* This value indicates how much 1 ml of original humate solution should be diluted to obtain a concentration of 0.136 g/litre.

An example is given in Table 131 of the method used in calculating the dilution necessary to bring the original humate solutions to the chosen concentration.

If the carbon concentration in the original humate solution is lower than the chosen value, the solution should be carefully concentrated by evaporation on a water bath at a temperature not exceeding 40° C. The carbon determination is repeated on the evaporated solution.

The optical properties of humic acids can be characterized by a simpler method. Scheffer (1954) and Welte (1955) have shown that the ratio of the extinction E at the wavelengths 465 $m\mu$ and 665 $m\mu$ (the so-called $E_4:E_6$ ratio) is independent of the concentration of carbon in solution, and, by reflecting the steepness of the spectrophotometric curve, is a characteristic of humic acids from different soil types. It is thus unnecessary to bring the sodium humate solutions to a given carbon concentration and this makes the determination of optical density much easier.

With humic acids from soils of various types, we have obtained the following characteristic values of the $E_4:E_6$ ratio: for podzolic soils, about 5.0; for dark-gray forest soils, 3.5; for ordinary chernozems, 3–3.5; for chestnut soils, 3.8–4.0; for serozems, 4–4.5; for krasnozems, about 5. For fulvic acids, the $E_4:E_6$ ratio lies between 6 and 8.5.

If in the rapid method of determining the humus composition the yield of humic acids is low, the analytical procedure may be limited to measuring the $E_4:E_6$ ratio. However, clear differences in these ratios are only obtained for humic acids from different soil types. The optical properties of humic acids from soils which are genetically similar are better characterized by spectrophotometric curves taken between the wavelengths 726 and 465 $m\mu$.

The character of the optical density curves and also of the $E_4:E_6$ ratios indicates that the degree of condensation in the aromatic nets of carbon atoms in humic acids increases on passing from podzolic soils to chernozems while the aliphatic side chains simultaneously decrease, whereas the opposite tendency is observed on passing from chernozems to chestnut soils and to serozems.

The aromatic part of the humic acid molecule has hydrophobic properties, whereas the side chains contain groupings with hydrophilic properties. The predominance of one or the other part determines the hydrophilic nature of the humic acid as a whole (see Chapter 2, section "The structure of the humic acid molecule"). This supposition is confirmed by determining the coagulation (precipitation) threshold of humic acids, which also characterizes the nature and properties of this group of substances.

THE DETERMINATION OF THE COAGULATION (PRECIPITATION) THRESHOLD OF HUMIC ACIDS

The solutions used for measuring the optical properties are also used for this determination. The electrolyte used for coagulating humic acids is CaCl_2 ; the concentration of the solution is such that the final concentration of CaCl_2 in the humate solution is from 1 to 20 m eq.

The experimental procedure is as follows. The coagulating electrolyte is a solution of 6.66 g anhydrous CaCl_2 in 1 litre of distilled water. Increasing volumes of this solution, from 0.05 to 1 ml, are added to a series of test-tubes and the volume of liquid in each tube is made up to 1 ml with distilled water. Five millilitres sodium humate solution containing 0.136 g/litre carbon are added to each tube, so that the total volume in each tube is 6 ml.

To facilitate adding the correct amount of CaCl_2 to each test-tube, Table 132 gives the volumes of CaCl_2 solution and of distilled water per 5 ml of humate which should be added to the test-tube for each final concentration of CaCl_2 in m eq./litre.

The working CaCl_2 solution and distilled water are added from 2 or 5 ml micro-burettes (see Table 132); aliquots of sodium humate are taken with a 5 ml pipette. It is essential that the solutions are delivered in the order: CaCl_2 solution, water, humate solution.

After adding the humate solution, the tubes are stoppered with rubber bungs and shaken. The time (in hours) and the corresponding amounts of electrolyte (in m eq) are recorded for the following stages:

- (a) The beginning of coagulation as indicated by the appearance of turbidity in the originally transparent solution.
- (b) Complete coagulation, when the solution above the precipitate becomes transparent and colourless.

For comparison, the results for complete coagulation are given in meq. CaCl_2 per litre of humate solution after 4 hours. In many instances, humates are only completely coagulated after longer periods of time, or are never completely coagulated; the appropriate observation is recorded.

Figure 78 illustrates the character of coagulation for humic acids from a chernozem and from a strongly podzolic soil, which differ markedly in their hydrophilic properties.

Data on the behaviour of humus substances towards electrolytes were given in Chapter 2 (see Table 21) and in Chapter 6.

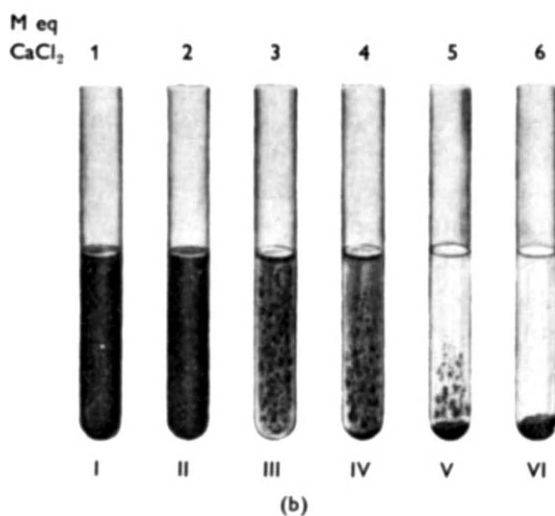
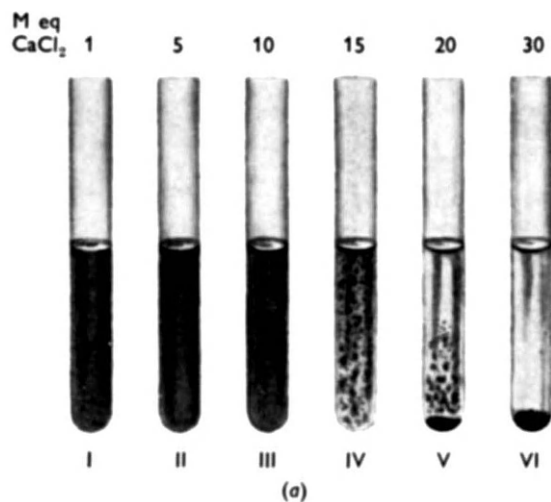


FIG. 78. Character of humic acid coagulation.

(a) Strongly podzolic soil: I, II, coagulation absent; III, appearance of turbidity; IV, appearance of flocs; V, precipitation of flocs; VI, incomplete coagulation: the flocs settled, but the solution remains coloured.

(b) Ordinary chernozem: I, coagulation absent; II, appearance of turbidity; III, appearance of flocs; IV, precipitation of flocs, light brown solution; V, precipitation of flocs, solution colourless; VI, complete coagulation, flocs settled, transparent colourless solution.

B. METHODS OF STUDYING THE NATURE OF HUMUS SUBSTANCES

ISOLATION OF HUMUS SUBSTANCES FROM THE SOIL AND THEIR PREPARATION FOR INVESTIGATION

Before the nature and properties of humic and fulvic acids can be investigated, they must be isolated from the soil.

The soil is prepared and decalcified (the extraction with ethanol–benzene may be omitted) and the humus substances extracted by repeated treatment with 0.1 N NaOH, following the procedures used in determining humus composition by Tyurin's scheme. Large amounts of soil are however necessary (1–5 kg) and correspondingly large volumes of liquid are obtained.

Humus substances may be extracted with sodium pyrophosphate–sodium hydroxide mixture in place of 0.1 N NaOH, as in the rapid determination of humus composition (see Section A of this chapter). This eliminates the decalcification stage, which is time consuming; after two or three treatments of large soil samples with this mixture, the humus substances are extracted completely.

The alkaline solutions are sucked off through a filter (porosity No. 4) held above the soil surface, combined, and the humic acids precipitated by the usual procedure. The acid solution is filtered through a No. 4 filter and used for subsequent isolation of fulvic acids.

If a super-centrifuge is available, the alkaline solutions are first sucked off through a coarse filter (No. 2 or 3), brought to pH 8.0–8.3 by adding H_2SO_4 and centrifuged at 15–25 thousand r.p.m.

The gel of humic acids is precipitated during acidification of the extract and after filtering off the acid solution, the gel is washed by decantation with distilled water. In order to decrease the ash content and remove impurities, the humic acids are re-precipitated. The dialysed gel of humic acids is air-dried by spreading it in a thin layer in Petri dishes. The air-dry humic acid preparations are carefully removed with a razor blade, thoroughly ground, passed through a 0.25 mm (or better 0.1 mm) sieve and stored in tightly stoppered test-tubes. The ash content of humic acid isolated by this procedure, with re-precipitation, does not usually exceed 3–4 per cent.

Fulvic acids are separated by passing the acid solutions from the humic acid precipitation through activated charcoal on a Büchner funnel; the fulvic acids are retained by the activated charcoal.

The activated charcoal is prepared by treating it for 24 hours with 10% HCl, washing away excess HCl with distilled water and grinding the moist charcoal to a paste in a porcelain mortar.

The activated charcoal containing absorbed fulvic acids is washed on the funnel several times with distilled water until the filtrate is weakly acid; the fulvic acids are removed from the charcoal by adding small amounts of cold 0.2 N NaOH. A part of the fulvic acid fraction is irreversibly fixed by the charcoal.

The alkaline solution is neutralized to pH 5.5–6.0 with sulphuric acid and concentrated to small volume *in vacuo* at 40–50° C. It is first dialysed at an initial potential of 80–100 V, until a negative reaction for OH ions is obtained (indicated by phenolphthalein). The current during dialysis should not exceed 100 mA. The concentrated dialysate of fulvic acids is poured in thin layers into Petri dishes and air dried. The fulvic acid preparations are ground, sieved and stored in tightly stoppered test-tubes. These preparations, which are readily soluble in water, mineral acids and alkalis are used for various analyses.

However, fulvic acids prepared by this procedure have a high ash content, often exceeding 10 per cent, apparently because intracomplex compounds with iron and aluminium are present. Using electrophoresis, we have shown that iron chelates are present in fulvic acid preparations (Kononova and Titova, 1961).

In recent years, ion-exchange resins (cation and anion exchangers) have been used for preparing humus substances and for studying their nature and properties. Their use in purifying humus substances has been described by Prokh (1961), and Hori and Okuda (1961). By combined use of appropriate cation and anion exchangers, it is possible to decrease the ash content of humus substances considerably. Ion-exchange resins are convenient because they may also be used to separate humic acids from fulvic acids without acidification of the alkaline soil extract, and to obtain sodium humates at given pH values (Prokh, 1961).

It is, however, necessary to select carefully the ion-exchange resin appropriate for work with humus substances, particularly since humus substances may be irreversibly absorbed by resins during filtering. Resins commonly used by investigators are: OH-Amberlite IRA-400, and H-Amberlite IR-120; Soviet resins used include the cationites KU-2 and KB-4, and the anionite EDE-10.

RAPID METHODS OF DETERMINING FUNCTIONAL GROUPS IN HUMUS SUBSTANCES

The methods generally used for determining functional groups are exhaustive methylation by methanol, dimethyl sulphate and diazomethane. As these methods are laborious and time consuming, simplified methods for determining functional groups deserve attention.

Stadnikov and co-workers (1929, 1934, 1935) have shown that the amount of barium hydroxide absorbed by humic acids is equivalent to the total carboxyl and phenolic hydroxyl groups in the humic acids. At the same time, only carboxyl groups react with calcium acetate. The difference between these two determinations represents the number of phenolic hydroxyl groups.

Syskov (1936) pointed out that the exchange reactions of functional group hydrogen with Ca(OH)_2 or Ba(OH)_2 are complicated by sorption of calcium and barium, and this should be taken into account when determining the total carboxyl and phenolic hydroxyl groups. In order to eliminate the possible difficulty caused by this sorption, Dragunova (1958) studied the reaction between humic acid and aqueous caustic alkalis, and developed a method for determining the total functional groups in humic acids. This method is described below.

Rapid methods of determining functional groups in humic acids (Dragunova, 1958)

The humic acid sample (about 0.1 g) is dissolved in 20 ml of 0.1 N NaOH in a 100 ml volumetric flask at room temperature. After half an hour, 10 ml of 0.5 N BaCl_2 are added, the solution is made up to the mark with CO_2 -free distilled water and the flask left overnight. A blank determination is also prepared at the same time.

Next morning, the clear solution is filtered off and a 20 ml sample titrated with 0.1 N HCl. The amount of barium combined with 1 g of humic acid is found from the difference between the titre of the blank and the titre of the sample.

Calculation

Humic acid sample (anhydrous, ash-free)	0.0734 g
Total volume of solution	100 ml
Volume of solution taken for titration	20 ml

Amount of humic acid corresponding to volume of solution

taken for titration 0.0147 g

Difference between blank titration and sample titration 1.18 ml

Therefore, 1 g humic acid corresponds with a titre of $\frac{1.18}{0.0147}$ ml of 0.1 M

HCl or 8.03 m eq Ba.

A check by determining barium gravimetrically in the precipitate gave a similar result to the above value.

The determination of carboxyl groups in humic acids
(Kukharensko, 1937a, b)

The method is based on the proposal by Stadnikov and co-workers (1929, 1934, 1935) that barium hydroxide could be used to determine the total functional groups, and calcium acetate to replace the hydrogen of carboxyl groups. The analytical procedure is as follows.

Air-dry humic acid (about 0.2–0.3 g) is weighed accurately into a beaker or a 200–250 ml flask with a ground glass stopper and 50 ml of 0.5 N calcium acetate solution, pH 6.8–7.0, are added. The contents of the flask are thoroughly mixed and left with occasional shaking for 4 days at room temperature. A blank with 50 ml of calcium acetate solution is prepared at the same time. The liquid is filtered through a fine filter into a dry receiver, and the precipitate is discarded without washing. An aliquot (10–15 ml) of the filtrate is pipetted into a 50–100 ml conical flask and titrated with 0.02 N NaOH, using a solution of phenolphthalein in alcohol as the indicator. The acetic acid titrated has been liberated by exchange reaction.

At the same time, calcium acetate solution from the control flask is titrated in order to determine the ratio between the calcium acetate solution and the sodium hydroxide solution, which is necessary for the calculation (blank determination).

The exchange absorption capacity is expressed in meq per 100 g anhydrous ash-free substance; 1 ml of 0.02 N NaOH is equivalent to 0.02 m eq Ca.

Calculation

Humic acid (calculated as anhydrous ash-free substance)	0.2262 g
Total volume of 0.5 N calcium acetate solution	50 ml
Volume of calcium acetate solution taken for titration	10 ml

Amount of humic acid corresponding to volume of solution
taken for titration

0.0452 g

Difference between blank titration and sample titration

11.07 ml

In proportion, 1 g humic acid combines with $\frac{11.07 \times 0.02}{0.0452} = 4.898$ meq

calcium.

Exchange capacity per 100 g anhydrous ash-free substance 489.8 meq.

METHODS OF FRACTIONATING HUMUS SUBSTANCES

Humic acids, fulvic acids and humatomelanic acids are commonly heterogeneous, and it is possible to separate them into fractions by methods which are based on their different nature and properties.

The methods to be selected for fractionation and for studying the individual fractions depend to a considerable extent on the aims of the investigator. One possible method is fractional precipitation from solution at different pH's; it has been used by Springer (1938), Schlichting (1953a, b) and Flaig, Scheffer and Klamroth (1955) for studying humic acids.

Tyurin (1940a) used fractional precipitation to separate fulvic acids into two fractions: one, precipitated by aluminium at pH 5.0–4.8 (α -fulvic acids); the second, not precipitated at this or other pH values (β -fulvic acids). These fractions differed in their colour and in the amount of exchangeable aluminium absorbed. Rydalevskaya and Tereshenkova (1961) fractionated fulvic acids by gradual precipitation with sesquioxides at various pH values of the medium.

Sowden and Deuel (1961) extracted substances from the B horizon of a podzolic soil and fractionally precipitated them with polyvalent cations and on cellulose columns.

Another method for fractionating humus substances uses the ultra-centrifuge (Beutelspacher, see Flaig, 1958a; Scheffer, Ziechmann and Schlüter, 1958).

Humus substances may also be fractionated with activated charcoal (Forsyth, 1947; Dragunov, 1951; Khan, 1951; Drozdova, 1955), on Al_2O_3 columns (Hock, 1937; Souci, 1938; Trojanowski, 1952, 1957a, b; Scholz, 1959; Scheffer, Ziechmann and Scholz, 1959; Hayashi and Nagai, 1960) and on starch columns (Kononova, Bel'chikova and Nikiforov, 1958).

We use partition paper chromatography and electrophoresis for fractionating humus substances.

Fractionation of soil humus substances by partition paper chromatography

Many investigators have used partition paper chromatography methods for fractionating humus substances of different origin. The method is based on the difference in the distribution of substances between two immiscible liquid phases—the aqueous phase, retained by the paper, and the moving phase of an organic solvent (n-butanol, phenol, chloroform, etc.) saturated with water.

Drops of the investigated mixture or of the heterogeneous substance are deposited on the strip of paper, and solvent passing through it separates the mixture into individual components or fractions, located in the form of spots or zones.

In some instances, the investigators did not resolve humus substances clearly into separate fractions (Ziechmann, 1954, see Scheffer and Ulrich, 1960; Krupskii and Laktionov, 1959; Coulson, Davies and Khan, 1959a, b). A more distinct resolution of humic acid into fractions has been described by Pavel, Koloušek and Šmatlák (1954), who used one-dimensional descending chromatography with pyridine-water as solvent. Hayashi and Nagai (1955) compared humic acids from soils and from peat, using one-dimensional ascending paper chromatography with 1.5 % NaOH solution as the solvent. Chromatograms showed three or four zones in ultra-violet light; the substances were extracted from these zones and the optical density and the non-hydrolysable residue determined. The authors established that the optical density and non-hydrolysable residue increased with the “maturity” of the humic acids.

Kroll (1958), Scharpenseel (1960) and Singh and Singh (1960) were able to separate natural humic acids from various soils and artificial humus-like substances into distinct zones on paper chromatograms. It was clear that the number of zones and their resolution depended both on the nature of the substance and on the method of chromatography.

We have used the method of circular partition paper chromatography for comparing humus substances from various soils (Kononova and Bel'chikova, 1960). The procedure was as follows. A sample of air-dry substance (0.2 g) was dissolved in 10 ml of 0.1 N NaOH; the pH of the humic acid and fulvic acid solutions was about 8.1–8.3.

Humus substances were chromatographed on 10–12 cm diameter circles of slow filtering paper. With a micro-pipette, one drop of known volume of the investigated substance was deposited in the centre of the paper circle and dried in the air. Knowing the carbon content of the solution,

the amount of carbon in the humus substances deposited on different parts of the chromatogram could be calculated.

A narrow strip—a wick—was cut from the edge to the centre of the circle and was bent back perpendicularly to the plane of the circle so that its free end dipped into the solvent, which ascended by capillary action. The solvent was a mixture of *n*-butanol, glacial acetic acid and water in the proportions 40:12:28; the mixture had a pH of 5.2, was homogeneous in specific gravity and was used in this form for chromatography.

The chromatogram was run at room temperature in a vapour compartment which was set up as follows. The paper circle with the dried drop of substance was placed over an open 9 cm Petri dish to which solvent had been added. The Petri dish was placed into another dish of 14 cm diameter, which was then covered with a lid. After 4–5 hours, the chromatograms were removed from the dishes and air-dried in a fume cupboard until the smell of solvent had disappeared. On the chromatograms of humic acids and fulvic acids from a chernozem, a sod-podzolic and a strongly podzolic soil, the following three zones appeared in ultra-violet light: A—remaining in the centre of the circle where the substance was deposited; C—peripheral, fluorescent; B—intermediate (Fig. 11, Chapter 2). The appearance of the chromatograms differed with different samples.

For studying the individual fractions of humus substances, the rings of zones B and C were cut out under ultra-violet light. The rings were cut in half and each half was folded and suspended so that the ends dipped into distilled water. The substances distributed throughout each half-ring were concentrated into the central part by the capillary rise of water; the half-rings were air-dried and the central parts cut out under ultra-violet light. The cut-out sections from all the chromatograms of any one preparation were combined and the substances were eluted from them by soaking in distilled water.

The aqueous solutions obtained were filtered through a filter (porosity No. 4) and concentrated in vacuo at 40–45° C to a small volume (5–8 ml). The solutions were poured into Petri dishes, where the liquid was allowed to evaporate at room temperature; the air-dry substances were removed from the dishes with a razor blade.

Substances in the central zone A were extracted in the following way. The zone was cut out, and if it contained fulvic acids, these were removed with water. Humic acids were extracted with 0.1 N NaOH solution and precipitated from the extract with HCl. The precipitate (gel) was washed by decantation and air-dried at room temperature. However, some of the substance remained absorbed on the paper.

The substances extracted from the individual zones were air-dried, ground in an agate mortar, passed through 0.1 mm mesh sieve and used in further investigations.

Investigations on the different fractions from the zones are described by Kononova and Bel'chikova (1960) and quoted in the present book (Chapter 2, in the section "The relationship between humic acids and fulvic acids").

*Fractionation of soil humus substances by paper
electrophoresis*

Electrophoresis is commonly used in biochemistry, microbiology and other biological sciences for separating mixtures of individual compounds (for instance, mixtures of amino acids or sugars) and for fractionating compounds of high molecular weight (for instance, proteins); it has also been used by many investigators for fractionating soil humus substances (Beutelspacher, 1952; Stevenson, Marks *et al.*, 1952; Pavel, Koloušek and Šmatlák, 1954; Thiele and Kettner, 1953; Scheffer, 1954; Scheffer, Ziechmann and Schlüter, 1955, 1959; Flaig, Scheffer and Klamroth, 1955; Welte, 1955; Coulson, Davies and Khan, 1959a, b; Noda and Iba, 1959; Jacquin, 1961).

The principle of the method is as follows. A mixture deposited on paper is separated into fractions by an electrostatic field applied across the paper by electrodes immersed in buffer solution. The number of fractions depends both on the nature of the mixture and on the electrophoresis method. For instance, if the electrophoresis is of short duration, using a slightly alkaline buffer (pH 8.6) and a potential of 110–300 V, natural and artificially prepared humic acids are divided into three or four fractions, one of which is fluorescent and only revealed in ultraviolet light. Using a higher potential and longer times, humus substances may be separated into a greater number of fractions (Kaurichev, Fedorov and Shnabel', 1960; Scheffer, Ziechmann and Schlüter, 1959).

Electrophoresis may be used to study complex formation in humus substances. Drozdova and Emel'yanova (1960) and Pospíšil (1962) have established by this method that humic acids and copper react to form both soluble mobile intracomplex compounds and immobile complexes.

We have used electrophoresis to fractionate humus substances and to study their complexes with iron. The instrument EFA-1 was used; it comprises a horizontal electrophoresis cell, a source of supply and a recorder (densitometer).

Solutions were prepared for electrophoresis as follows. Air-dry samples (0.01–0.02 g) of humus preparations were dissolved in enough 0.02 N NaOH to give a pH of 8–8.5 in the final solution. To complete the dissolution, the sample and solution were placed in beakers on a hot water bath; the carbon contents of the resulting solutions were determined.

Strips of slow-filtering chromatographic paper, 2.5 cm × 40 cm, were used in the electrophoresis. The humate solution was deposited by a calibrated micropipette on a marked starting line in the centre of the strip and dried in a stream of hot air. If the organic substances were light-coloured, several aliquots were deposited from the micropipette. After drying, the strips were quickly moistened with buffer solution and placed in the cell with their ends immersed in vessels containing the same buffer solution. Nine strips were placed in the cell simultaneously; the potential was about 20 V per cm width of the strip (500 V : 2.5 cm × 9). The conditions used in the electrophoresis are given in Table 133.

TABLE 133. CONDITIONS FOR ELECTROPHORESIS

Voltage, V		Current, mA		Fractionation time hours	pH of borate buffer
Initial	Final	Initial	Final		
500	460	20	42.0	1.5–2	8.6

When fractionation was complete, the strips were removed from the cell, rapidly dried in a current of hot air and examined by ultra-violet light. When humic acids (from a chernozem, from a sod-podzolic soil and from the humus-illuvial horizon of a strongly podzolic soil) and fulvic acids were used, three zones appeared on the electrophoretograms: A, a zone remaining on the starting line; B, a negatively-charged zone (moving towards the anode); and C, the most mobile zone, which was fluorescent. However, the distribution of the substances in the zones varied with different samples. A characteristic distribution of humus substances into fractions on the electrophoretograms is illustrated in Fig. 12 (Chapter 2).

As mentioned above, electrophoresis has been used by us to detect iron-humus complexes. For this purpose, the electrophoretograms were sprayed with 4 per cent potassium ferrocyanide ($K_4[Fe(CN)_6] \cdot 3 H_2O$) solution acidified with sulphuric acid; this destroys the complexes. This treatment causes a blue-green colour to develop on the strips where the complexes are located. The appearance of this colour at the start (in zone A) shows

that immobile iron-humus complexes are present. The development of the colour in zone B shows that mobile negatively-charged iron-humus complexes of the chelate type are present. We were able by this method to explain the tendency to form complexes with iron which is differently manifested in humic acids and fulvic acid from different soils (see the data in Chapter 4, section "The role of organic matter in forming the soil profile; forms of linkage between organic matter and the mineral part of the soil", and also Fig. 46).

THE USE OF INFRA-RED SPECTROSCOPY IN STUDYING THE NATURE OF SOIL HUMUS

Infra-red spectroscopy is now commonly used for investigating the chemical structure of substances. When infra-red light passes through a substance, it excites vibrations of atomic groups in the substance causing characteristic absorption bands to develop.

By this method it is possible to obtain information about the presence of various atomic groupings and functional groups in the substance without disturbing its chemical integrity.

A number of authors have described the use of infra-red spectroscopy for studying soil humus substances and synthesized humus-like substances (Kasatochkin and Zil'berbrand, 1956; Kasatochkin, Kononova and Zil'berbrand, 1958; Karavaev and Budyak, 1960; Orlov *et al.*, 1962; Kumada and Aizawa, 1958; Kobo and Tatsukawa, 1959; Ziechmann, 1958; Scheffer, Ziechmann and Pawelke, 1958; Wright and Schnitzer, 1959; Goulden and Jenkinson, 1959; Jenkinson and Tinsley, 1960; Scharpenseel and Albersmeyer, 1960; etc.).

It appears that the light absorption curves obtained in the infra-red region from soil humus substances are, like the curves in the visible and ultra-violet regions, without sharply developed maxima and minima; this may be explained by their high molecular weight and heterogeneity. Similar infra-red spectra for humic acids from different soils and peats have been recorded, confirming that the principles of their structure are the same.

The use of infra-red spectroscopy for studying humus substances is complicated by some displacement of the bands characterizing a given atomic group from the corresponding values given by Bellamy (1956). Difficulty in deciphering infra-red spectra is also caused by the presence of nitrogen-containing groupings, for the bands corresponding to these are superimposed on bands characteristic of other groups. For instance, the

absorption at $6.1\ \mu$ may be due not only to stretching vibrations of $C=C$ double bonds (indicating the presence of aromatic groups and conjugated $C=O$ groups) but also to stretching vibrations of $C=N$ in heterocyclic nitrogen compounds, to bending vibrations of NH in primary and secondary amines and to bending vibrations of NH_2 in amides.

From the published data quoted above, it is possible to assign the following absorption ranges to the corresponding groups.

3030 cm^{-1} ($3.3\ \mu$)	aromatic CH
2941–2857 cm^{-1} ($3.4\text{--}3.5\ \mu$)	aliphatic CH_2 and CH_3
1710–1695 cm^{-1} ($5.89\text{--}5.9\ \mu$)	vibration of carboxyl $C=O$ (carbonyl) in aromatic and aliphatic acids
1639–1600 cm^{-1} ($6.1\text{--}6.25\ \mu$)	stretching vibrations of conjugated $C=C$ carbon bonds; $C=O$ in quinones
1375–1370 cm^{-1} ($7.28\text{--}7.3\ \mu$)	aliphatic CH_2 and CH_3
1300–1163 cm^{-1} ($7.69\text{--}8.6\ \mu$)	$C-O$ of aromatic ethers
1160–1060 cm^{-1} ($8.62\text{--}9.43\ \mu$)	$C-O$ of cyclic and aliphatic esters and alcohols

The bands which sometimes appear at 6.1 and $6.5\ \mu$, corresponding to the stretching vibrations of atomic groups containing nitrogen, have already been discussed above.

So if an aromatic carbon net is present in soil humus substances, it may be characterized by the bands at: $3030\ \text{cm}^{-1}$ ($3.3\ \mu$), $1639\text{--}1600\ \text{cm}^{-1}$ ($6.1\text{--}6.25\ \mu$); some authors (Flaig, 1958b; Orlov *et al.*, 1962) also use the band at $6.7\text{--}6.8\ \mu$ for this characterization. It should be noted that the aromatic HC groups at $3.3\ \mu$ are difficult to detect in soil humus substances because of the high degree of substitution in the net of aromatic carbon.

On account of the complex nature of humus substances, many workers have compared the infra-red spectra of these substances with the spectra of their destruction products. This type of investigation shows much promise; such data are given by Wright and Schnitzer (1959), Scharpenseel and Albersmeyer (1960) and Orlov (1962).

The method of preparing the substances for investigation is very important. Our samples were prepared in the form of discs by pressing $4\text{--}5\ \text{mg}$ of the investigated substance with $1\ \text{g}$ of KBr . The spectra were measured on a recording infra-red spectrophotometer, type IKS-14 (double beam), with $NaCl$ and LiF prisms. However, under these experimental conditions humic acid samples from a chernozem, fulvic acids from a sod-podzolic soil, and newly-formed humus substance isolated from an actinomycetes culture did not show distinct bands in the short wave region. We therefore

limited ourselves to examining the spectra in the range 5–10 μ , obtained by recording with the NaCl prism (see Figs. 14 and 17). By carefully dispersing and drying the humus substance being investigated before pressing with KBr, it is possible to detect the absorption at 3030 cm^{-1} (3.3μ) corresponding to the vibration of the aromatic CH groups (Kasatochkin and Zil'berbrand, 1956; Kononova, 1956).

C. METHODS OF STUDYING THE DYNAMICS OF ORGANIC MATTER IN THE SOIL

The methods just described for investigating the organic part of the soil are designed to characterize the humus of different soil types and soil sub-types. Under different land use (forest, meadow, arable) within the same soil variety, differences in humus composition are only slight or are not observed at all.

The research worker faces still greater difficulties when characterizing the humus status of soils under different crops. Here the general nature of the organic matter transformations can be followed by determining both the humus and nitrogen contents and by estimating the root mass. An indication of the amount of newly-formed humus substances in the soil can be obtained by determining the free forms of humic acids.

Differences in the humus composition of reclaimed soils (in the humic and fulvic acid contents and in the ratio of these acids) can only be established when the soils differ markedly in the degree of improvement and in the amount of organic matter added (see Tables 96 and 98).

Boratyński and Wilk (1962) developed a method in which humus substances were extracted from the soil by various reagents, beginning with milder (NaF , NH_4F) and finishing with more powerful ($\text{Na}_4\text{P}_2\text{O}_7$, NaOH) extractants. This method may prove useful in characterizing the composition of humus not only from different types of soil but also from soils of the same type but with differing degrees of improvement.

Methods recommended for studying the dynamics of soil organic matter are given below.

Estimation of the aerial mass and roots of plants (Pankova, 1960)

The aerial mass and leaf-fall of plants are sampled from an area of $25 \times 25\text{ cm}$ ($1/16\text{ m}^2$) in 3–5 replications, air-dried and weighed. The results are expressed in grams per square metre and in quintals per hectare.

For estimating the roots, Kachinskii's method (1925) is used, as modi-

fied by Savvinov and Pankova (1942). After recording the botanical composition of the area to be sampled, the soil profile is exposed and described. The freshly prepared profile wall is divided by horizontal lines into genetic horizons or into 10 cm layers, and on it two vertical lines 25 cm apart are marked out. In this way a soil column of area 25×25 cm is marked out with sub-divisions into horizons.

The soil in each horizon is sampled separately. It is recommended that a 25 cm square should be used to help in taking an accurate sample of the soil. The correctness of the cut in the walls of the profile can be checked by inserting the square into the cavity. After the sample has been taken, a cavity remains in the wall of the soil profile which exactly corresponds to the volume of the soil column removed.

The plant residues and roots are washed from each soil sample by repeated decantation, the water being poured off through a 0.5 mm mesh sieve to retain the floating roots. When all the plant material has been separated and washed with water, it is divided into the following fractions: (1) living roots; (2) partly decomposed roots; and (3) well humified plant residues.

The fractions are separated as follows. The washed material is placed in a basin, covered with water and stirred. Light, undecomposed and slightly decomposed plant residues float to the surface; they are poured off through a sieve, taking care not to catch the living roots which, because of their somewhat greater density, settle to the lower layers. When the material is again covered with water and stirred, half-decomposed residues entangled in the living roots are liberated and float to the surface; they are collected and added to the main part of this fraction.

The living roots remain in the water, settling slowly, and the strongly humified plant residues fall rapidly to the bottom. The contents of the basin are stirred, and not allowing the living roots to settle, these latter are poured off with the water through a small sieve without disturbing the humified residues which have settled at the bottom of the basin. This fractionation is repeated until the living roots are completely separated.

The strongly humified material remaining at the bottom of the basin is collected separately. All the fractions isolated are air-dried and weighed: moisture, ash, carbon (by Knop's method) and nitrogen (by Kjeldahl's method) are determined in each of these fractions.

The ratio of living roots to dead plant residues may serve as an index of the intensity of humification (Pankova, 1952; Glotova, 1956). When the humification is intense, the quantities of dead plant residues left in the soil are small, whereas when it is retarded, this fraction accumulates. This

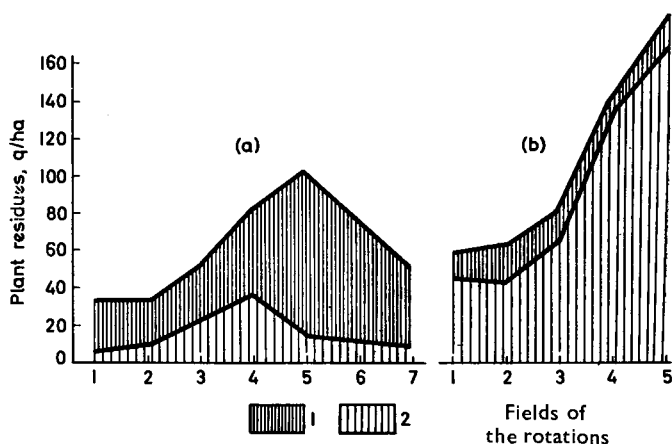


FIG. 79. Plant residues in the 0–40 cm layer of a chestnut soil under different crops (Glotova, 1956). (a) Unirrigated; (b) irrigated. (1) Dead plant residues; (2) living roots.

is illustrated by Fig. 79 from the work of Glotova (1956). She determined the fractional composition of roots and plant residues under two different managements: under irrigation where humification is intense; and without irrigation, where microbiological processes are clearly retarded.

Biochemical analysis applied to the study of plant residues in the soil

Sometimes the research worker is interested in the biochemical composition of the aerial mass, the plant leaf fall and the root systems. For such investigations, the biochemical analysis of plant materials as described in the textbooks by Kizel' (1934) and by Belozerskii and Proskuryakov (1951) may be used.

In our experience, it is advisable in such investigations to determine the following groups of substances in the plant mass.

1. Substances extracted by 1:1 ethanol–benzene mixture; the material is extracted in a Soxhlet apparatus for 12–20 hours.

2. Hemicelluloses are determined by hydrolysing the residue from 1 with 2% HCl for 3 hours in a Koch's apparatus. Reducing sugars are afterwards determined in the hydrolysate; the amount of reducing sugars multiplied by 0.9 represents the hemicellulose content.

3. Cellulose is determined in the residue from 2 by hydrolysing it with 80% H_2SO_4 at room temperature. The mixture is then diluted with 15 volumes of water and hydrolysed for 5 hours in a Koch's apparatus; sugars

are determined in the liquid. The amount of sugars multiplied by 0.9 gives the cellulose content.

4. Lignin is determined from the loss on ignition of the plant material remaining after 3.

In certain instances it is advisable to determine in addition water-soluble organic matter, total and protein nitrogen, starch and tannins. Suitable methods are described in the textbooks mentioned above.

Often the research worker wishes to find out if humus substances are present in the isolated material. Partly decomposed material may be further oxidized and humified when humus substances are extracted with 0.1 N NaOH, and to avoid this, we recommend that a "milder" method, extraction with 0.1 M sodium pyrophosphate solution of pH about 8.5, is used. This method has been developed by Drozdova (1959a) for similar investigations with peats.

The dynamics of humus and nitrogen in soils

When studying the dynamics of humus and nitrogen in soil, the sampling method is very important. A sufficient number of soil samples should be taken and analysed to establish the variability of the field, and from this, the number of soil samples required to give a statistically representative sample of the field is calculated.

This is illustrated by an example from our investigations. It was noticed at the Dokuchaev Agricultural Institute in the central chernozem belt (Kamennaya Steppe) that the soil between the forest belts had a higher humus content than the soil in the open steppe. In order to make sure that this conclusion was correct, we collected a large number (20–30) of soil samples because of possible variations in the soil. The carbon content of each was determined and the data were subjected to a mathematical treatment, the results of which are given in Table 134.

In this table, $\sigma = \sqrt{\frac{\sum \chi^2}{n-1}}$, $v = \frac{\sigma \cdot 100}{M}$ and $P = \frac{m \cdot 100}{M}$ where $\sum \chi^2 =$ = the sum of the squares of the deviations from the mean, n = the number of samples, M = the arithmetical mean and m = the mean square error.

When the variability of the field has been established, the minimum number of samples necessary for collecting a mean soil sample is given by the formula

$$n = \frac{v^2 t^2}{P^2}$$

where n = the number of replications and t = the index of significance.

TABLE 134. ORGANIC CARBON CONTENT IN SOIL (0–20 cm horizon)

Land use and crop	Investigated area ha	Number of samples analysed	Organic carbon % soil weight $M \pm m$	Standard deviation σ	Coefficient of variation ν	Coefficient of variation of the mean P %
Arable land between forest belts	14	30	5.16 ± 0.08	0.453	8.78	1.6
Arable land in open steppe	5	20	4.62 ± 0.06	0.259	5.61	1.2

As can be seen from Table 134, with the large number of samples taken (30), an accuracy ($P = 1.2$ – 1.6 per cent) has been obtained which considerably exceeds the usual accuracy of analysis.

In similar investigations, the accuracy is usually limited to $P = 5$ – 8% , so that taking $P = 5\%$ and $t = 2$ (which corresponds to a significance $v = 95\%$), it can be shown that the number of samples can be decreased to twelve $\frac{(8.78^2 \times 2^2)}{5^2}$ for the field with large variability (between the forest belts) and to five $\frac{(5.61^2 \times 2^2)}{5^2}$ for the field with less variability (open steppe).

The carbon content of the soil between the forest belts exceeds that of the soil in the open steppe (both soils under similar managements and crops) by 0.54 per cent. Using the formula

$$\frac{M_1 - M_2}{\sqrt{m_1^2 + m_2^2}} = t$$

we can establish the significance of this figure:

$$t = \frac{5.16 - 4.62}{\sqrt{0.08^2 + 0.06^2}} = \frac{0.54}{\sqrt{0.01}} = 5.4.$$

As can be seen, the value of t is much greater than 2. Therefore the higher humus content of the soil between the forest belts, compared with the soil of the open steppe, is significant, even though the difference is small.

Methods of studying the composition of organic matter in soil solutions (Aleksandrova, 1960)

Investigations of the composition of organic matter in aqueous extracts and in the soil solution has been hampered by the lack of generally applicable methods, and soil scientists have limited their investigations mainly to the determination of total organic carbon.

Recently developed methods of investigation, including the various kinds of chromatography, may lead to an understanding of the qualitative composition of these substances. Procedures are described below that are applicable to solutions extracted from soils and peats by the method of Kryukov (1947). To obtain these solutions, water is added to the soil until it is at 60 per cent of the full moisture holding capacity; peats are brought to 100 per cent moisture capacity. The moist samples are left to stand at room temperature and after 5–7 days, the solutions are squeezed out in a press under a pressure of 125–150 kg/cm². The solutions (and also the extracts) are completely clarified by centrifuging and filtering through a Chamberlain candle or through membrane filters. The solutions are concentrated *in vacuo* at a temperature of 40° C, before being applied to the paper.

We have examined the qualitative composition of compounds of an aromatic nature, low-molecular weight organic acids and amino acids using partition paper chromatography. Appropriate “marker” substances were deposited on the chromatographic paper at the same time as the solution being investigated. The compounds were identified after chromatographic separation and development by comparing the location and colour of the spots from the solution investigated with those from the “markers”.

Substances of an aromatic nature. Before determining the substances in this group, the solution must be concentrated 40–50 times *in vacuo* at 40° C. A small volume (1–2 ml) of the solution is carefully mixed with anhydrous sodium sulphate in a small porcelain dish. The mixture is dried in a current of hot air (40–50° C), transferred to a flask and extracted two or three times with ether.

The ether extracts are evaporated to small volume in a current of cold air and 50–150 μ l deposited on chromatographic paper with a calibrated micropipette.

We separate substances by one-dimensional descending chromatography on slow filtering paper over a period of 24 hours. The solvent is a mixture of n-butanol, glacial acetic acid and water (40:12:28). Two

solutions were used in succession to develop the chromatogram: (1) a mixture of 25 ml 0.3% sulphanilic acid solution in 8% HCl and 1.5 ml 5% NaNO_2 solution; (2) 20% Na_2CO_3 solution.

Low-molecular-weight organic acids. The preparation of the solution for determining this group of substances is the same as for substances of an aromatic nature. Low-molecular-weight organic acids are isolated from the solution by two or three extractions with ether acidified with sulphuric acid.

The ether extracts are evaporated in a current of cold air and a volume of 100–200 μl is deposited on the chromatographic paper. The chromatograms are run for 40 hours using as solvent n-butanol saturated with formic acid and water; the ratio of the components is 18:2:9. The chromatograms are developed with 0.04 per cent alcoholic bromo-cresol green brought to approximately pH 7.5 with 0.1 N alkali (the solution is an intense blue colour).

Amino-acid composition of the solutions. The solutions were concentrated 40–50 times *in vacuo* and chromatographed directly after concentration and also after hydrolysis with 6 N HCl for 20 hours at 105° C.

In the first instance a small amount (1 ml) of concentrated solution was evaporated to dryness in a current of hot air at a temperature of 40–45° C and the residue was dissolved in 10 per cent *iso*-propyl alcohol; 200–300 μl of this solution were deposited on the chromatogram.

For the hydrolysis, enough concentrated HCl was added to 3 ml of the concentrated solution to make the normality of HCl in the final volume 6 N. The solutions were transferred to 15–25 ml glass tubes, the tubes sealed, and placed in a thermostat at 105° C for 24 hours.

When the hydrolysis was complete, the contents of the tubes were diluted with water and filtered through filter paper moistened with water to remove insoluble residue. The residue was washed several times on the filter and the filtrate and washings were evaporated almost to dryness in a porcelain dish on a water bath at 35–40° C. To remove the excess HCl, the solution was evaporated 5 or 6 times, each time adding new portions of water. The final volume of hydrolysate was made up to 2–5 ml.

The solvent used for separating the amino acids was the organic phase of the mixture n-butanol, glacial acetic acid and water in the proportions 4:1:5. The developing reagents were 0.4 per cent ninhydrin in butanol or an alcoholic solution of isatin. The chromatograms were run for 40 hours at first, and then after drying, for another 24 hours.

Results from these determinations of the composition of organic compounds in soil solutions are given in Chapter 2 in the section "Organic substances of individual nature" (see also Fig. 1).

Procedures used in the partition paper chromatography of organic compounds of an individual nature are described in a number of books (Belozerskiĭ and Proskuryakov, 1951; Block, LeStrange and Zweig, 1952; Kramer, 1958; Paech and Tracey, 1960). We have also used the procedures described in the following articles for determining separate groups of substances: organic acids—Shkolnik (1953); aromatic compounds—Zaprometov (1954) and Bray, Thrope and White (1950); amino acids—Boyarkin (1956, 1958).

Further development and improvement of chromatographic methods should be directed towards the quantitative determination of the individual organic substances in soil solutions.

Among the procedures recommended in the literature for quantitative chromatography the following deserve attention: measurement of the colour intensity of the spots with a densitometer; extraction of the substances from the chromatogram with appropriate solvents and determination of their amounts by chemical and optical methods.

A SHORT SURVEY OF THE MAIN SOIL TYPES OF THE USSR

by N. N. Rozov

In this survey characteristics of the main soil types of the USSR, particularly those soils for which data are provided in M. M. Kononova's book, are given in brief. The reader can obtain more detailed information from the literature cited in the list of publications.

Within the USSR, two systems of soil-geographical zones, fairly clearly differentiated from each other, are distinguishable. A system of horizontal soil zones is characteristic of the great plains of the USSR. In the mountainous region a separate system of vertical soil zones is distinguished.

On the plains of the USSR there are five main horizontal soil zones: (1) the zone of tundra soils; (2) the zone of podzolic and frozen-taiga soils; (3) the zone of chernozems and gray forest soils; (4) the zone of chestnut soils; (5) the zone of semi-desert and desert soils. In addition, in the south (Transcaucasus and Central Asia) several subtropical regions with zheltzozems, krasnozems, cinnamonic soils, gray cinnamonic soils and serozems, representing parts of soil zones situated outside the USSR, are distinguished. In the following account cinnamonic soils, gray cinnamonic soils and serozems are included in the zone of semi-desert and desert soils.

The zone of tundra soils

This zone extends in a narrow belt along the Arctic coast of the European part of the USSR and Siberia. The total area of the zone is over 170 million hectares (about 8 per cent of the area of the USSR).

The tundra climate is characterized by low temperatures, long, cold winters, short summers and low precipitation (150–300 mm). The characteristic features of soil formation in the tundra are associated with the presence in the soil not far below the surface of permanent frost, which impedes the penetration of atmospheric precipitation into the lower layers. Therefore, tundra soil is excessively moist throughout its depth, and during the summer period its temperature is considerably lower than the temperature of the air.

The soil-forming rocks in the tundra zone are mainly glacial deposits. In eastern Siberia, eluvium and diluvium of primary rocks also occur. The soil-forming process develops under vegetation consisting of mosses, lichens and scrub. The annual growth increment of the vegetation is not great, hence the addition of organic residues to the soil is small.

In tundra soils, the decomposition of the organic residues is slow due to the weak activity of micro-organisms. On the whole, the humus content of tundra soils is low; compounds of fulvic-acid type predominate and the humus substances are very mobile. Data characterizing the humus of tundra soils are given in Table 55.

Typical tundra soils have a peat-humus horizon of small thickness below which, in anaerobic conditions, a moist gley horizon occurs. In the latter horizon reduction of ferric compounds to ferrous forms predominates; the process takes place with the participation of soluble organic compounds leached from the surface layer.

In addition to the described tundra soils, which are characterized by a low accumulation of organic matter, peat-boggy soils characterized by the accumulation of plant residues occur in the southern part of the tundra zone. As a rule, the peat layer of these soils is of small thickness. In places where summer thawing of the soil penetrates to a greater depth, in light sandy soils in the river valleys, peculiar tundra-like podzolized soils, usually formed under tundra scrub and possessing a weakly expressed podzolized horizon, occur. In the tundra, mainly reindeer husbandry is practised; in the southern part, agriculture is also possible (particularly the cultivation of vegetable crops).

The zone of podzolic and frozen-taiga soils

This zone occupies more than 700 million hectares (more than 31 per cent of the area of the USSR) and together with the adjoining region of mountain-podzolic and mountain-frozen-taiga soils of Siberia, occupies about 1200 million hectares, representing over 50 per cent of the total area of the USSR.

Podzolic soils occur in the East European, West Siberian and Far Eastern parts of the zone. The climate of these regions is moderately cold and adequately moist. The annual atmospheric precipitation varies from 300–600 mm, decreasing towards the east. A characteristic feature is that precipitation exceeds evaporation; as a result of this, soil formation takes place under conditions of high moisture and leaching.

The soil-forming rocks are extremely diverse; the most widespread are the glacial and old alluvial deposits; in the Far East, eluvium and diluvium of primary rocks predominate. Podzolic soils develop under dark coniferous forests of taiga type (spruce, Scots pine, fir, cedar) with a ground cover of mosses. The surface of the soil is covered by forest litter consisting of fallen leaves; water percolating through the forest litter acquires an acid reaction due to the presence of organic acids formed during the decomposition of the organic residues. Acid solutions affect the upper mineral soil horizons and give rise to podzolization.

Podzol formation is a complex physico-chemical and biochemical process. It consists of the dispersion of soil colloids and the disintegration of the secondary soil minerals. The occurrence of a descending water current promotes the translocation from the upper to the lower horizons of colloidal hydroxides of aluminium and iron, colloidal aluminosilicates and a number of other elements, including essential plant nutrients. Under these conditions, quartz grains are resistant to decomposition and their relative accumulation is observed in the podzolic horizon (A_2), which is of whitish colour. Products leached from the podzolic horizon are partially removed by the groundwater and partially retained by the underlying (illuvial) horizon (B); below this horizon occurs slightly changed soil-forming rock, usually designated horizon C.

In the majority of podzolic soils there occur side by side with the podzolic process different degrees of development of the sod process leading to the formation of a humus horizon (A_1), to structure formation in this horizon and to the accumulation of plant nutrients. The appearance in the forest of grass vegetation promotes the development of the sod process. The sod process proceeds more intensively in the southern part of the taiga-forest zone (in the belt of southern taiga and deciduous-coniferous forests); it is much less evident in the central and northern part. A number of soil characteristics change, in particular, the nature of the humus, depending on the intensity of the podzolic and sod processes. Podzolic soils have a very low humus content; in the humus, substances of the fulvic-acid type predominate; the humic acids resemble fulvic acids. The humus substances are very mobile. With the development of the sod process the activity of micro-organisms in the soil increases and the soils become more humified. In the humus the content of humic acid increases; the humic acids become more complex (data characterizing the nature of the humus of podzolic soils are given in Table 54 and also in Chapters 2 and 6).

Within the podzolic-soil type are distinguished: (1) *sod-podzolic soils*,

(2) *podzolic soils*, (3) *podzolic illuvial humus soils* and (4) *gley-podzolic soils*, depending on the degree of development of the sod process.

Sod-podzolic soils are characterized by a soil profile with horizons $A_0-A_1-A_2-B-C$. The forest litter (A_0) forms a thin layer (3–5 cm). The thickness of the humus horizon (A_1) is also not very great (10–15 cm) and the humus content is 3–4 per cent. The absorption capacity of this horizon is up to 15–20 m eq per 100 g soil in loamy soils; in the composition of the absorbed cations hydrogen and aluminium predominate and absorbed calcium and magnesium amount to 6–8 m eq. The podzolic horizon (A_2) is almost devoid of humus and is poor in mineral colloids; the absorption capacity decreases to 4–5 m eq per 100 g soil. The illuvial horizon (B) has a higher absorption capacity again, which can be attributed to the high content of clay particles and mineral colloids.

Podzolic soils have a profile: A_0-A_2-B-C . The humus horizon (A_1) is not usually developed; those soils having a clearly defined podzolic horizon are termed *podzols*.

Podzolic illuvial humus soils are similar to podzolic soils in the general structure of the profile but differ from them by the considerable accumulation in the illuvial horizon (B) of leached-in humus (up to 3–5 per cent). They occur mainly on light-loamy and sandy soil-forming rocks.

Gley-podzolic soils are developed in the cis-tundra belt on loamy rocks. They are characterized by a peat horizon (A_0) 10 cm deep, and in the podzolic horizon (A_2) evidence of surface gleying can be detected; this is associated with the increased surface moisture resulting from the peculiarities of the climatic regime.

Frozen-taiga soils, which are distinguished as a separate soil type, are developed under light coniferous (or deciduous) taiga of central and eastern Siberia under conditions more continental and more severe than those under which podzolic soils are formed; in these soils permafrost occurs near the surface. They are characterized by a weakly differentiated soil profile of small thickness, freezing (cryogenic) phenomena in the active layer, the absence of podzolization and only slight accumulation of humus.

In conjunction with podzolic soils, podzolic-boggy and boggy types of soil are widely distributed.

Podzolic-boggy soils (sod-podzolic-gley and peat-podzolic-gley) develop under conditions of temporary excessive moisture. They have a surface humus or peaty horizon overlying a podzolic horizon, and a gleyed illuvial horizon.

Boggy soils are formed under continuous, excessively moist conditions. Their characteristic feature is the accumulation in the surface horizon of

organic matter, which is only slightly humified because of the restricted aeration. Below this occurs the gley horizon containing ferrous compounds which give it a characteristic greenish-gray colour. Among boggy soils are distinguished: high-moor (*Sphagnum*), transitional and low-moor (grassy) soils depending on the composition of the vegetation. Peat, peat-humus and humus soils are distinguished according to the degree of decomposition of the organic matter in the upper soil horizon. The soils of the podzolic and frozen-taiga zone are not much used for agriculture. The most reclaimed are the sod-podzolic soils of western regions of the USSR. In this zone, large areas remain under forest and bogs. Under the conditions of a long period of agricultural utilization and fertilizer application, podzolic soils undergo great changes; the thickness of the humus horizon increases, acidity decreases and soil structure improves.

The zone of chernozem and gray forest soils

This zone stretches in a continuous belt from the western frontier of the USSR to the Altaï foothills.

This zone is widest, about 300 km, in the West European part of the USSR; it extends to the Black Sea and the Azov Sea and to the foothills of the Caucasus and embraces north Crimea. In west Siberia and Kazakhstan, it narrows to 150 km; in central and east Siberia chernozems and gray forest soils occur only in depressions between the mountains. The total area of the zone is 260 million ha (12 per cent of the area of the USSR).

The great extent of the zone from east to west explains the diversity of climatic conditions. The annual precipitation in the west and in the Cis-caucasus is up to 500–600 mm; towards the east (particularly in Siberia) it decreases to 350 mm and below.

The parent rocks are varied; in the west there is a predominance of loess and loess-like loams, which alternate with eluvium and diluvium of primary rocks towards the east.

Gray forest soils develop in the northern part of the chernozem zone—under deciduous forest in the European part of the USSR and under birch and birch–larch forests in Siberia. They differ essentially from sod-podzolic soils by the more clearly defined and thicker humus horizon and by the absence of a continuous podzolic horizon, which is replaced by interspersions of quartz and by the presence of a peculiar nut-like structure. The humus content of gray forest soils is high (compared with sod-podzolic soils) with an increased content of humic acids. The humus becomes more stable (see Table 54, data of Chapter 6).

Gray forest soils are distinguished from one another by a number of chemical characteristics. Thus, in *dark-gray forest soils* of loamy composition the humus content is up to 6–8 per cent or more. The absorption capacity amounts to 30–40 m eq per 100 g soil; in the composition of the absorbed cations calcium and magnesium predominate and the content of hydrogen and aluminium ions is low. The thickness of the humus horizon is usually 40–50 cm; the decrease in humus in the soil profile is gradual. At the surface the soil reaction is slightly acid (pH 6.5); in the lower part of the humus horizon the reaction is more acid (pH 5.5); here, an interspersed of whitish silica occurs and penetrates into the upper part of the illuvial horizon (B), which has a nut-like prismatic structure.

The humus content in true *gray forest soils* decreases to 6–4 per cent, and in *light-gray forest soils* to 3 per cent. The thickness of the humus horizon also decreases correspondingly and signs of podzolization are more clearly defined. The general morphology of the soil profile of gray forest soils can be represented as follows:

A₁–A₁A₂–A₂B–B–C–Ck; the last horizon usually occurs at a depth of 1.5–3.0 m and contains calcium-carbonate concretions in the form of tubes and mycelia.

With regard to the origin of gray forest soils there is, at present, no unanimous opinion, which is explained by the multi-stage nature of their development. According to Korzhinskiĭ's hypothesis, gray forest soils develop as a result of the degradation of steppe chernozems with the encroachment on them of forest vegetation; consequently, the humus of gray forest soils is partly of steppe origin.

Other investigators (Taliev, Williams, Tyurin) believed that the formation of gray forest soils from sod-podzolic soils was possible with the replacement of coniferous forest by deciduous forest and with the development of a rich grass vegetation under the forest canopy.

The second type of soils in this zone are *chernozems*. As was shown by the classical investigations of Dokuchaev, and Kostȳchev, these soils are formed under various grasses – graminaceous steppe vegetation. The specific climatic conditions of the chernozem zone, where the moistening of the soil by atmospheric precipitation is balanced by evaporation from the surface, produce only slight leaching of the calcium carbonate and provide conditions for the accumulation of organic matter in the form of humus compounds. The latter are represented mainly by humic acids, which are of a fairly complex nature (data given in Chapters 2 and 6). In the various sub-types of chernozems the content and composition of the humus differs (see Table 54).

The characteristic features of chernozems are: (1) the presence of a well-developed, dark, humus horizon with a humus content, in the surface layer, of 4–18 per cent and with a gradual decrease of humus with increasing depth; (2) the presence of a carbonate horizon with concretions of calcium carbonate occurring at various depths; (3) a high absorption capacity of up to 40 and even 60 m eq per 100 g soil, depending on the humus content and the mechanical composition; (4) the saturation of the colloidal part of the soil with bases (mainly calcium).

This chernozem-type soil is divided into several sub-types:

Podzolized chernozems with a deep (120–170 cm) carbonate horizon and with the presence of an interspersed quartz in the profile are distinguished. These soils usually occur under forest vegetation. The humus content in podzolized chernozems varies from 5 to 9 per cent and the thickness of the humus horizon is 45–60 cm.

Leached chernozems are formed under vegetation consisting of *Gramineae* and other herbaceous species. They also have a lower carbonate horizon (at a depth of 70–110 cm), are rich in humus (7–11 per cent) and the thickness of the humus horizon is 50–80 cm.

In *typical chernozems* the features of the chernozem type of soil formation are most completely expressed. The humus content at the surface ranges from 4–5 per cent (in Ukrainian chernozems) to 10–12 per cent (in Transvolga and Cisaltai chernozems). Correspondingly, the thickness of the humus horizon ranges from 120–140 cm to 60 cm; this serves as a basis for designating the Ukrainian chernozems “thick” and the Transvolga chernozems “fertile”. Calcium carbonate occurs in the lower third of the humus horizon—in the zone of root development.

Ordinary chernozems are formed under vegetation consisting of *Gramineae* and other herbaceous species and have some of the features associated with a dry climate. The humus content usually varies within 6–9 per cent and the thickness of the humus horizon ranges from 90 cm in the west to 50 cm in the east of the zone. Effervescence with HCl is usually observed in ordinary chernozems in the central part of the humus horizon. At a depth of 2–4 m small amounts of gypsum and readily soluble salts can be found, marking the boundary of soil moistening.

Southern chernozems, occupying the southern boundary of the chernozem zone, are formed under more arid climatic conditions. The humus content varies from 6 to 4 per cent and is sometimes as low as 3.5 per cent. The thickness of the humus horizon decreases from 70 to 40 cm on passing towards the east. In the composition of absorbed cations, magnesium begins to play an essential role in the lower part of the soil profile, and at a

depth of 150–200 cm gypsum and readily soluble salts are found. In addition to the 5 sub-types of chernozems mentioned there are distinguished at the present time a number of other sub-types and varieties whose systematic position is not finally determined. In this category are the *mycelium-carbonate chernozems* developed in the warmest regions of the chernozem zone—the area adjoining the Azov Sea and the Ciscaucasus. *Residual-carbonate chernozems* are formed on rocks rich in carbonate. *Solonets-like chernozems* are usually developed on saline, soil-forming rocks and often occur in complexes with solonetses.

Within the chernozem zone a separate type of *meadow-chernozem soil* is distinguished; this soil is formed under the conditions of a flat relief; groundwaters occur near surface and characteristics of the gleying process are found in the lower part of the profile. Some of these soils have clearly defined solonets features.

The majority of chernozem soils, because of their high humus content, large reserve of nutrients and good structure, possess a high potential fertility.

The zone of chernozems and gray forest soils is the zone most utilized for agriculture. In the western part of the USSR, within the Ukraine, the area under cultivation is very large and, in places, amounts to over 80–90 per cent of the territory. Beyond the Ural Mountains the degree of utilization of the zone for agriculture decreases, but still amounts to 40–50 per cent.

The zone of chestnut soils

This zone occurs to the south of the zone of chernozems and gray forest soils and stretches in a narrow belt along the northern coastal region of the Black Sea and Azov Sea, includes the lower reaches of the rivers Volga and Ural, and occupies large areas of Kazakhsk SSR. In the eastern part of the USSR, chestnut soils occur in depressions between the mountains in the Altai–Sayansk region and in the south-eastern part of Trans-Baikal. The total area of the zone is over 120 million ha (more than 5 per cent of the area of the USSR); chestnut soils occupy about 70 per cent of the area of the zone and solonetses and other soils, up to 30 per cent.

The climatic conditions of the zone are varied, although on the whole they are characterized by dryness and also, in the eastern regions, by severeness. The annual precipitation ranges from 180–200 to 300–350 mm, with a decrease towards the east and south. Evaporation from the surface considerably exceeds the amount of precipitation, particularly in eastern regions.

The vegetation is poor, particularly in the southern part of the zone; there is a predominance of *Artemisia-Stipa-Festuca sulcata* and *Artemisia-Festuca sulcata* associations. Chestnut soils are sub-divided into *dark chestnut soils* and *light chestnut soils* (in some cases *true chestnut soils* are distinguished in addition). Dark chestnut soils are formed under a more dense *Artemisia-Gramineae* plant cover and are distinguished by a higher humus content (3–4 per cent in the surface layer) with a thickness of the humus horizon of 40–50 cm. Light chestnut soils are developed under a sparse *Gramineae-Artemisia* plant cover of semi-desert type; their humus content is as low as 2 per cent and the thickness of the humus horizon decreases to 30 cm. While retaining certain characteristics typical of chernozems, the humus of chestnut soils (particularly light chestnut soils) has a lower content of humic acids (see Table 54); in their nature these humic acids differ from the humic acids of chernozem (see data in Chapters 2 and 6).

The characteristic feature of chestnut soils is their solonets-like nature, particularly clearly defined in light chestnut soils. The development of the solonets-like nature in these soils is associated with the following phenomena. During the hot summer there is a dry period during which time, owing to the capillary rise of the soil solution and to the intensity of evaporation in the upper soil horizons, some accumulation of readily soluble salts is observed in the soil profile. These accumulations include sodium salts, which give the soil solution a slightly alkaline reaction and promote peptization of the colloidal part of the soil. In slightly solonets-like chestnut soils the solonets features are revealed by a noticeable consolidation of the lower part of the humus horizon; in strongly solonets-like chestnut soils this consolidation is more considerable and the upper part of the humus horizon loses its stable structure and becomes dispersed. All these features are clearly expressed in soils of *solonets* type, which are widely distributed among the chestnut soils and also among brown, desert-steppe soils.

The profile of a typical solonets usually consists of two main horizons: the upper horizon—loose, structureless (solodized), humified at the surface, from which fine, colloidal particles are leached by the action of descending currents of atmospheric water; the lower horizon—compact, columnar (solonets-like) into which colloidal particles are deposited. *Crusted solonetses*, *medium-columnar solonetses* and *deep-columnar solonetses* are distinguished, depending on the depth of the columnar horizon, and *solonchak solonetses*, *solonchak-like solonetses* and *leached solonetses*, depending on the depth of occurrence of readily soluble salts.

These features are very important for characterizing solonetses in connexion with their reclamation. During their development solonetses may be transformed either into solonets-like steppe soils or into solods, which already contain no readily soluble salts, have almost no absorbed sodium and possess a clearly differentiated soil profile. The zone of chestnut soils and solonetses is used for agriculture mainly in its northern part. On dark chestnut soils agriculture is possible without irrigation. Light chestnut soils are almost without exception covered with *Artemisia* steppe and in Kazakhstan are a centre for livestock rearing.

The zone of semi-desert and desert soils

This is the most southerly soil zone of the USSR. It occupies the southern part of Kazakh SSR on the territory of the Central Asiatic republics (Turkmen, Uzbek, Tadzhik and Kirgiz) entering Azerbaïdzhan SSR. The total area of the zone occupies about 220 million ha (about 10 per cent of the total area of the USSR), of which about 56 million ha are occupied by sands and about 10 million ha by solonetses, solonchaks and takyrs. The annual precipitation is 120–250 mm.

In the recent past all the soils of this zone (with the exception of aeolian sands, solonchaks, solonetses and takyrs) were regarded as belonging to a single type of soil formation — serozem. As a result of recent studies there are distinguished among the soils of semi-deserts and deserts: (1) *brown desert-steppe soils*, which are formed in the northern part of the zone under *Artemisia* vegetation with an admixture of *Gramineae*; (2) *gray-brown soils* previously termed “structural and gypsum-bearing serozems”, which are formed mainly on the products of weathering of close-grained rocks under sparse *Salsola-Artemisia* vegetation; (3) *true serozems*, associated with the occurrence of vegetation of the desert-ephemeral type; they are formed, as Rozanov showed, under a heat regime approaching the sub-tropical. Adjoining serozems in the Kura-Araksın Lowland are gray cinnamonic soils.

For *brown desert-steppe soils* a low content of humus (1.5–2.0 per cent), a very low content of humic acids in the humus, a clear manifestation in the profile of signs of a solonets-like nature and of solodization are characteristic. *Gray-brown desert soils* are characterized by an extremely low humus content (less than 1 per cent), by a distinct solonets-like nature and by the accumulation of gypsum in the profile. *Serozems* have a slightly differentiated and deep profile, containing from 1 per cent humus (light serozems) to 3–4 per cent (dark serozems), and are distinguished by more intensive weathering within the profile and by a high carbonate content.

The high activity of micro-organisms during periods of adequate moisture is the characteristic feature of serozems; hence, humus substances are rapidly drawn into the biological cycle and this imparts features of instability to the humus of these soils. Data characterizing the nature of the humus of soils of semi-deserts and deserts are given in Table 54 (see also Chapters 2 and 6).

Among gray-brown desert soils are distinguished the so-called takyr-like soils and takyrs. The process of takyr formation is observed in deserts on clayey plains under the influence of stagnant alkaline surface-waters. It is expressed by the formation of compact crusts on the soil surface often inhibiting the growth of plants and allowing only the growth of algae.

Meadow-serozem soils and solonchaks are observed in river valleys with high groundwater levels, in depressions and around the edges of basins. Solonchaks are soils with a considerable content of readily soluble salts in the surface horizons. The formation of solonchaks is observed under arid and dry climatic conditions in those places where groundwaters can rise to the surface through the soil capillaries and are evaporated with the consequent accumulation of salts. Maritime and continental solonchaks are distinguished, depending on the origin of the salts in the groundwaters. The former, when occurring along the sea coasts, are supplied with sea water (solonchaks in the coastal region of the Caspian Sea); the continental solonchaks, which are supplied with groundwaters from the land, acquire salts as a result of the weathering of various rocks and have a very diverse salt composition.

Large areas of loose sands within the examined zone are often blown by the wind; they possess no soil cover, or soil formation is weakly expressed in them.

The zone of semi-desert and desert soils with the presence of a temperature regime favourable for agriculture (particularly in its southern sub-tropical regions) is characterized by great moisture deficiency. Agriculture is only developed, therefore, where conditions for artificial irrigation exist. In the natural state, the territory of the steppe zone is utilized for pastures. Under the influence of irrigation, under conditions which allow the deposition of irrigation detritus, characteristic irrigated soils of high fertility develop.

The soils of moist sub-tropical regions

Two moist sub-tropical regions are distinguished in the USSR—Adzharsk-Abkhazsk (Black Sea) and Lenkoransk, which occupy small areas but have an enormous importance as a centre for the cultivation of the

most valuable sub-tropical crops—tea, citrus, tung oil tree (*Aleurites fordii*), etc.

The *Adzharsk-Abkhazsk* moist sub-tropical region extends from Sochi to Batum on the east coast of the Black Sea. Being protected from the north and east winds by the mountains of the Great and Little Caucasus, this region is distinguished by a very warm and extremely moist climate with an annual sum of precipitation in some places of over 2000 mm. The natural type of vegetation (at the present, very little has survived) was shady deciduous forests, of varied composition, with large numbers of lianes. Under these forests in the northern part of the region, *zheltozems* and *zheltozem-like podzolic soils* with large ferrous concretions and gleying in the lower part of the profile were formed on Quaternary clay deposits. In the southern part of the region on red-coloured clayey products of the primary crystalline rocks and crystalline conglomerates, *krasnozems* were formed.

In moist and sub-tropical regions the weathering processes proceed intensively and lead to the accumulation, in the soils and in the underlying thick crust of weathering, of aluminium and iron hydroxides; the latter give the soils a bright red colour. *Krasnozems* have, at the surface, a well-developed or less developed humus horizon under which a podzolic horizon is often observed. The conditions of soil formation (surface leaf-fall, high moisture) favour the formation of humus substances of the fulvic-acid type (see Table 54). The humic acids in their nature and properties are similar to fulvic acids (data on this problem are given in Chapters 2 and 6).

The *Lenkoransk* moist sub-tropical region is situated in the south-west coastal region of the Caspian Sea and is protected from the cold winds by the Talýshsk Ridge. With regard to the climate, the Lenkoransk region is somewhat drier than the Black Sea region; here the summer is drier. *Zheltozems* and *zheltozem-like podzolic soils* are predominant in the soil cover.

The soils of mountain regions of the USSR

Mountain regions of the USSR occupy an enormous area—over 670 million ha, which represents more than 30 per cent of the area of the USSR. The distinguishing features of all mountain soils are their small thickness, good drainage, considerable stoniness and susceptibility to destructive erosion in the case of disturbance of the natural plant cover. All the processes of soil formation known for the plains are also observed on mountains, only often in peculiar “mountain” modifications.

In the USSR the following types of mountain soils are distinguished:

(a) in the northern mountain regions — mountain-tundra soils, mountain-frozen-taiga soils, mountain-podzolic soils and mountain-gray forest soils; (b) in the southern mountain regions — mountain-meadow soils, mountain-brown forest soils, mountain cinnamonic soils, mountain chernozems, mountain chestnut soils and mountain serozems.

The high mountain-desert soils occurring above 300 m in Pamir occupy a special place in the soil classification. Under mountain conditions, soils of different types of soil formation follow one another in succession and form a system of vertical soil zones with increasing latitude of the locality. The reason for this succession is the decrease in temperature and increase in the amount of precipitation with increasing altitude. Here, however, there is no complete analogy with the phenomenon of the horizontal zonality of soils despite the general similarity of these phenomena.

The mountain regions of the USSR are reclaimed very little for agriculture. Southern mountain regions with mountain-steppe soils are reclaimed more than the soils of other regions. Here, on mountain chernozems, mountain cinnamonic soils, mountain chestnut soils and dark mountain serozems, unirrigated agriculture is extensively developed. Southern mountain regions which have a predominance of mountain-brown forest soils and mountain-meadow soils are less utilized for agriculture, since forestry and, on the mountain pastures, livestock rearing are of great importance here. Finally, northern mountain regions with mountain-podzolic soils and frozen-taiga soils have a small percentage of arable land due to the severe climate and the small population of these regions.

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